The recovery of aluminium utilising the Donnan Membrane Process

by

Moletsane Mophethe

Thesis presented in partial fulfilment

of the requirements for the Degree

of

MASTER OF ENGINEERING

(CHEMICAL ENGINEERING)

in the Faculty of Engineering

at Stellenbosch University

Supervisor

Professor V.L Pillay

Co-Supervisor

Professor S.M Bradshaw

December 2018

DECLARATION

By submitting this thesis electronically, I declare that the entirety of the work contained therein is my own, original work, that I am the sole author thereof (save to the extent explicitly otherwise stated), that reproduction and publication thereof by Stellenbosch University will not infringe any third party rights and that I have not previously in its entirety or in part submitted it for obtaining any qualification.

Date: *December 2018*

PLAGIARISM DECLARATION

1. Plagiarism is the use of ideas, material and other intellectual property of another's work and to present is as my own.
2. I agree that plagiarism is a punishable offence because it constitutes theft.
3. I also understand that direct translations are plagiarism.
4. Accordingly all quotations and contributions from any source whatsoever (including the internet) have been cited fully. I understand that the reproduction of text without quotation marks (even when the source is cited) is plagiarism.
5. I declare that the work contained in this assignment, except where otherwise stated, is my original work and that I have not previously (in its entirety or in part) submitted it for grading in this module/assignment or another module/assignment.

Student number: ……..

Initials and surname: ……..

Signature: ……..

Date: ……..

Abstract

The recovery of aluminium from Water Treatment Residuals (WTRs) is both an economic and environmental advantage. Its economic attractiveness lies in the fact that the aluminium can be recycled and reused in municipal potable water treatment plants, which consequently reduces their operational costs. The source of this metal is from a coagulation salt called Alum that is subsequently precipitated after flocculation occurs. The precipitated sludge is discarded into water bodies such as rivers and lakes, as well as land fill sites. Large concentrations of aluminium have been found to be toxic to both wildlife and aquatic life. In the case of humans, research has indicated a strong correlation between high aluminium concentrations and contracting Alzheimer's disease.

Three current methods that exist to recover this aluminium are namely: acid digestion, alkalization and Donnan Dialysis. While both digestion and alkalization have been shown to recover up to 80% of the aluminium, research has shown that the recovery is highly non selective as organics have been found to be recovered in the process as well. The aims and objectives of this project are to identify and investigate the optimal flow rates and concentrations that maximize the recovery of aluminium ions from Water Treatment Residuals using Donnan Dialysis. Secondly, to establish if Donnan Dialysis can selectively recover aluminium ions whilst simultaneously rejecting organics.

In order to achieve these objectives, a laboratory scale Donnan Dialysis rig was set up. Experimental runs were performed on synthetic feed in order to quantify the effects of the manipulated variables (feed flow rate, sweep flow rate, feed concentration and sweep concentration) on the recovery of aluminium ions with the final objective of maximizing aluminium ion recoveries. Once the effects were quantified, further experimentation was conducted using real Water Treatment Residuals (WTRs) from Blackheath treatment plant. The objective of this was to establish if Donnan Dialysis could selectively recover aluminium ions whilst rejecting organics.

It was found that water transport in the system from the feed to the sweep side diluted final aluminium ion concentrations. Further investigation revealed that the water flux was linearly proportional to the concentration of acid used. The higher the acid concentration, the higher the water flux. In addition, acids at the same concentrations with higher Van't Hoff factors attributed to a higher water flux than using those with a smaller Van't Hoff factor.

Based on experimental results from synthetic feed utilizing a Box Behnken design, a statistically significant second order model was fitted, allowing optimisation of the operating parameters. It was found that a combination of low feed concentrations and moderate acid concentrations (with flow rate having no effect) were found to yield the highest recoveries of aluminium. The highest recovery was found to be 98%.Statistical analysis at a confidence interval of 95% revealed that the feed concentration was found to be the most significant parameter. Both sweep concentration and feed flow rate were found to be statistically insignificant.

For the real WTR feed analysis, two acids concentrations were used for digestion, namely 0.5M and 0.05M HCl. The stronger acid was found to breakdown the sludge more efficiently. The starting concentration of aluminium in the 0.5M sludge was found to be 600 mg/L while that of the 0.05M acid was 300 mg/L. The concentration of organics in the stronger acid digestion was also higher than that of the weaker.

Donnan Dialysis was found to selectively recover aluminium whilst rejecting organics by up to 97% in the first 24 hours of operation. The maximum recovery of aluminium using real WTRs feed was found to be 97%. When synthetic feed was used, a 98% recovery of aluminium was obtained in the first 24 hours of operation.

Donnan Dialysis is a promising alternative for the recovery and reuse of aluminium from municipal potable water treatment residuals. The two limiting factors of the technique are the slow kinetics of the process and that the subsequently recovered aluminium requires further concentration before it can be directly reused in the water treatment process.

Opsomming

Die herwinning van aluminium uit waterbehandelingoorblyfsels (WBOs) het beide ’n ekonomiese en omgewingsvoordeel. Die ekonomiese aantreklikheid lê in die feit dat die aluminium herwin en hergebruik kan word in munisipale drinkbare waterbehandelingsaanlegte, wat gevolglik die operasionele kostes verminder. Die bron van hierdie metaal is van ’n koagulering sout, genaamd aluin, wat vervolgens presipiteer nadat flokkulering plaasvind. Die gepresipiteerde slyk word weggegooi in watermassas soos riviere en damme, asook vullisterreine. Groot konsentrasies aluminium is toksies vir beide natuurlewe en akwatiese lewe. In die geval van mense, het navorsing getoon dat daar ’n sterk korrelasie tussen hoë aluminiumkonsentrasies en die opdoening van Alzheimersiekte is.

Drie metodes bestaan om hierdie aluminium te herwin: suurvertering, alkalisasie en Donnan Dialise. Terwyl beide vertering en alkalisasie al gewys het dat dit tot 80% van die aluminium kan herwin, het navorsing bewys dat die herwinning hoogs nie-selektief is as gevolg van die organiese komponente wat ook in die proses herwin word. Die mikpunt en doelstellings van hierdie projek is om die optimale vloeitempo’s en konsentrasies te identifiseer en ondersoek, wat die herwinning van aluminiumione van waterbehandelingoorblyfsels sal maksimeer deur Donnan Dialise te gebruik. Tweedens, om vas te stel of Donnan Dialise selektief die aluminiumione kan herwin terwyl dit terselfdertyd organiese komponente verwerp.

Om hierdie doelstellings te bereik, is ’n laboratoriumskaal Donnan Dialise opstelling opgerig. Eksperimentele lopies is gedoen op sintetiese voer om die effek van die gemanipuleerde veranderlikes (voervloeitempo, veevloeitempo, voerkonsentrasie en veekonsentrasie) op die herwinning van aluminiumione met die finale doel om die aluminiumioon-herwinning te maksimeer. Sodra die effekte gekwantifiseer was, is verdere ekperimentasie gedoen deur gebruik te maak van werklike waterbehandelingoorblyfsels (WBOs) van ’n Blackheath behandelingsaanleg. Die doel hiervan was om vas te stel of Donnan Dialise aluminiumione selektief kan herwin, terwyl dit organiese komponente verwerp.

Dit is vasgestel dat wateroordrag in die stelsel van die voer na die veekant finale aluminium-ioonkonsentrasies verdun. Verdere ondersoek het bekendgemaak dat die watervloed liniêr proporsioneel aan die konsentrasie van suur gebruik, is. Hoe hoër die suurkonsentrasie, hoe hoër die watervloed. Sure met dieselfde konsentrasies wat hoër Van’t Hoff faktore het, het ook bygedra tot hoër watervloed, eerder as die met ’n kleiner Van’t Hoff faktor.

Gebaseer op eksperimentele resultate van sintetiese voer wat ’n Box Behnken ontwerp gebruik, is ’n statisties beduidende tweede orde model gepas, wat optimering van die bedryfparameters toelaat. Dis gevind dat ’n kombinasie van lae voerkonsentrasies en gematigde suurkonsentrasies (met vloeitempo wat geen effek het nie) die hoogste opbrengs van herwinde aluminium gehad het. Die hoogste herwinning was 98%. Statistiese analise by ’n vertrouensinterval van 95% het gewys dat die voerkonsentrasie die mees beduidende parameter was. Beide veekonsentrasie en voervloeitempo is as statisties onbeduidend gevind.

Vir die werklike WBO voer analise is twee suurkonsentrasies vir vertering gebruik, naamlik 0.5 M en 0.05 M HCl. Dis gevind dat die sterker suur die slyk meer effektief afbreek. Dis gevind dat die begin konsentrasie van aluminium in die 0.5 M slyk 600 mg/L was, terwyl dít van die 0.05 M suur 300 mg/L was. Die konsentrasie van organiese komponente in die sterker suur vertering was ook hoër as dié van die swakker.

Dis gevind dat Donnan dialise selektief aluminium herwin terwyl dit organiese komponente afgekeur het, tot en met 97% in die eerste 24 uur van bedryf. Die maksimum herwinning van

aluminium wat werklike WBO voer gebruik, is gevind om 97% te wees. As sintetiese voer gebruik is, is ’n 98% herwinning van aluminium verkry in die eerste 24 uur van bedryf.

Donnan Dialise is ’n belowende alternatief vir die herwinning en hergebruik van aluminium uit munisipale drinkbare waterbehandelingoorblyfsels. Die twee beperkende faktore van die tegniek is die stadige kinetika van die proses en dat die herwinde aluminium steeds verdere konsentrasie vereis voor dit direk in die waterbehandelingsproses hergebruik kan word.

Dedication

I dedicate this work to my loving mother Mme Kuena Mophethe who has been there for me from my first breath on this Earth. I would not be where I am today if it was not for her unconditional love, support and guidance. For that I am eternally grateful.

This thesis is also dedicated to those who have been dealt a poor hand in life. Persevere, persevere. Victory awaits you over the horizon. Take it, it is yours.

"We *cannot change the cards we are dealt, just how we play the hand"- Randy Pausch*

Acknowledgments

I would like to express my sincere gratitude and appreciation to the following for their countless assistance throughout my masters journey:

- I thank the Lord Jesus Christ for the strength and guidance.
- My mother Mme Kuena Mophethe for her unwavering motivation and support.
- My supervisors Professor Pillay and Professor Bradshaw for their guidance and advice.
- The technical staff, Mr Alvin Peterson, Anton Cordier, Brent and Jos Weerdenburg for their assistance with the manufacturing and setting up of my experimental rig.
- Mrs Hanlie Botha, Levine Simmers and Jaco van Rooyen for assisting and advising on the appropriate procedures to follow for analytical techniques.
- My loving fiancée Rethabile Myoli for her compassion, patience and always being there with a shoulder to lean on.
- The Water Research Commission (WRC) for the financial support and opportunity to undertake this project.
- Mrs Francis Layman and Juliana Steyl for always having time to assist me with purchase orders and project logistics.

Table of Contents

Table of figures

List of tables

Chapter 1 Introduction and background

1.1 Problem in context and motivation

The scarcity of potable water is a global crisis. In South Africa, the scarcity and decrease in water quality is exacerbated by rapid urbanisation, the mining sector, the pollution of rivers and other water bodies, and in more recent years the lack of adequate rainfall (Rand Water, 2018).

In an attempt to mitigate water pollution and meet national water demands, some municipalities and their associated provinces have resorted heavily to water restrictions (Western Cape) as well as the recycling of polluted water through the use of municipal water treatment plants (Cloete, 2017). This drive has proven to be very successful. With the increasing pressure on municipal water comes the need to operate water treatments plants ever more efficiently.

A large scale municipal potable water treatment process consists of three main stages: primary, secondary and tertiary treatment (Asano, 1988). The primary stage consists of the screening, coagulation, flocculation and sedimentation of material. The secondary stage focuses on disinfection by either chlorine, UV light or ozone. Lastly, the tertiary stage involves the final processing of the purified water such as pH adjustment (Asano, 1998).

Screening is designed to remove floating debris and grit which may damage mechanical equipment or inhibit some biological processes from taking place (American Water Works Association, 2003). The screening equipment of choice is usually barracks, which are parallel bars or rods of about 20-150 mm in diameter. Another alternative is the use of bar screens, these are perforated plates usually about 10 mm or less (American Water Works Association, 2003).

In order to remove dissolved organic matter and colloids once screening has taken place, a treatment combination of coagulation and flocculation is done. Coagulation is achieved by neutralizing the charges of dissolved organic matter and colloids through the use of a coagulant (Mihelcic et al., 2010). A coagulant is a chemical which is added in order to destabilize particles and accomplish coagulation. Ferric sulphate, ferric chloride, aluminium sulphate (Alum) and aluminium chloride are widely used coagulants. The resulting sludge that is precipitated is discarded in landfill sites or water bodies such as rivers and lakes (Mihelcic et al., 2010). One of the major disadvantages of this approach, in particular with aluminium salts is that large concentrations of aluminium are toxic to the flora and fauna, as well as human life (Mihelcic et al., 2010). The link between exposure to high concentrations of aluminium by ingestion and neurodegenerative diseases such as Alzheimers disease (AD), Amyotrophic Lateral Sclerosis (ALS) and Parkinsons dementia has been the subject of scientific debate for decades, with researchers such as Kawahara and Kato-Negishi (2011) supporting that a link does exist. The dilemma of it being ethically unacceptable to dose humans with aluminium has made validating this difficult. However researchers have since relied on historical accounts of high aluminium concentrations in drinking water and the resulting consequences to the surrounding population as well as the testing on animals to further understand the relationship.The first relationship between aluminium and memory disorder was recorded and reported by Spofforth (1921). In 1951 Chusid et al. (1951) demonstrated that the intra-cerebral administration of aluminium induced epilepsy in monkeys. Lastly, in 1988 there was an accidental contamination of aluminium in drinking water in Cornwall, UK. The 20,000 affected people were found to exhibit symptoms indicative of cerebral impairment, such as loss of concentration and short term memory in a 10 year study conducted by Altmann et al. (1999). The World Health Organization developed a

tolerable weekly intake of aluminium to be 1mg/kg of body weight, where anything higher should be a cause for concern (Cotruvo, 2017).

A further disadvantage to the continued purchase and disposal of Alum, from the outlook of water treatment plants, is the major operational cost associated with purchasing the Alum. The City of Cape Town has 12 water treatment works ranging in treatment capacity from 3 ML/day (Constantia Nek) to 500 ML/day (Faure) as cited by Tredoux (2016). In total the treatment works produce roughly 48,000 ML per month. The average dosing of Alum in the treatment works is estimated at 75.3 mg/L and the price of purchasing Alum is roughly R2,100 per ton (Tredoux, 2016). Given this, the cost for coagulation per month is R7, 600, 000 and R91,000,000 per annum in only 1 of the 9 provinces in South Africa.

Given the considerable expenses incurred by the water treatment plants in purchasing Alum and the potential toxic impact of disposing of Alum in landfill sites and water bodies, water treatment plants and researchers have looked into the possible ways in which the Alum found in the precipitated sludge after flocculation and coagulation has occurred, also known as Water Treatment Residuals (WTRs), can be recovered and reused. The possibility of recovering and reusing the Alum would mean that it would no longer be dumped in land fill sites and water bodies, this would mitigate the potential harmful impacts of aluminium on the environment. In addition to this, it would greatly save water treatment plants in monthly operational expenditure.

In recent years, two solutions for the recovery of Alum from WTRs have been investigated, namely acid digestion and alkalization (Prakash, 2004). Acid digestion makes use of sulfuric acid to recover Alum from the WTRs at a pH range of 1-3 to recover 70-80% of the Alum (Prakash, 2004). Alkalization, on the other hand, utilizes sodium hydroxide and lime to recover Alum from the Water Treatment Residuals at a pH range of 11-12 while recovering 80% of the Alum (Prakash, 2004). The shortcomings of acid digestion and alkalization were found to be that while they were successful in recovering up to 80% of Alum from the precipitated sludge, the recovery was highly non-selective (Prakash, 2004). This meant that in addition to the recovered Alum, organic compounds were recovered as well. Over time, the recycling of this Alum into the coagulation process would lead to organic build up which would be undesirable.

Given the undesired outcome that both alkalization and acid digestion were found to be non-selective in their recovery of Alum, a third option which utilized relatively new technology was considered, Donnan Dialysis technology. Donnan Dialysis is a membrane driven process. It utilizes the counter diffusion of ions through an ion exchange membrane. The process is driven by an electrochemical potential gradient across the membrane (Prakash et al., 2004). The process is performed counter-currently with the objective of taking dilute solutions and concentrating them into a small volume (Prakash et al., 2004). There are two types of membranes processes available for Donnan Dialysis. The first is cationic exchange and the second is anionic exchange (Davis, 2001). In both processes a membrane separates two compartments containing two different electrolytic solutions. The cationic membrane is essentially a polymer with fixed negative charges dispersed uniformly within the film (Davis, 2001). The counter ions which are positively charged are free to exchange with other positively charged ions from the solutions in both compartments, while the negative counterparts of the positive ions in the solutions are not permitted to interact with the membrane due to their charge (Davis, 2001).

The advantage of the Donnan Dialysis approach over the acid digestion and alkalization process is that it allows the selective recovery of Alum while rejecting organics. In addition to this, according to the thermodynamic laws that govern this process, Prakash (2004) suggested that it should theoretically be possible to obtain recoveries which are higher than 80% (higher than alkalization and acid digestion).

In traditional membrane processes, such as Ultrafiltration, Nanofiltration and Reverse Osmosis, previous studies have found that in general due to the membranes being pressure driven, high energy requirements are often needed for separation (Chen, 2016). In addition to this, the blockage of membrane pores and fouling takes place due to organics being present in the feed stream, and thus ultimately stopping the process (Chen, 2016). Chen (2016) specifically conducted studies on ultra and nano filters. He found that ultra-filters could only successfully reject aluminium ions by 14%. Nano filters proved to be more successful and their rejection rates were found to be 96%, meaning that multi valent aluminium ions could be successfully intercepted and concentrated. The problems, however, were found to be that, while aluminium rejection was high, it was extremely non selective and organics were also found to be concentrated with the aluminium as well. In addition to this, due to the presence of organics, fouling took place in the system which in turn drastically reduced the flux of the system (Chen, 2016).

The author considered Donnan Dialysis as it did not have some of the more common shortcomings of these processes, such as: having high energy requirements due to the separation being pressure driven, and as a bi-product, the clogging up and ultimate fouling of the membrane. The separation obtained through Donnan Dialysis is not pressure driven and is only a function of initial concentration and activity. It relies on the use of a cationic exchange membrane and ionic transfer which is driven by electrochemical potential.

Given this, the objective of this project is to investigate whether aluminium can selectively be recovered from potable water treatment residuals using the Donnan Dialysis approach.

1.2 Problem statement

The aluminium from Water Treatment Residuals is currently disposed of in land fill sites or water bodies. The high concentrations pose a danger to the environment and human life (Mihelcic et al., 2010). The current possible methods of recovering the aluminium such as acid digestion and alkalization have proved to be highly non selective in their extraction and recovery process. Traditional membrane methods such as Ultrafiltration and Nanofiltration have been found to be energy intensive due to the large pressures required to operate them. These high pressures also result in the ultimate clogging up of pores and fouling due to organics present in the feed stream. A new cationic exchange membrane process named Donnan Dialysis will be investigated. Due to the process being driven by an electrochemical potential instead of pressure, the shortcomings of traditional membrane processes are avoided. Secondly, Donnan Dialysis allows for selective recovery of aluminium ions while simultaneously rejecting organics, this presents an advantage over acid digestion and alkalization.

1.3 Research objectives

The aim of this study is to determine if aluminium can be obtained from Water Treatment Residuals with both high selectivity and high recovery with the use of Donnan Dialysis (DD). In order to meet this aim, the following objectives need to be achieved:

1. To identify and investigate the optimal flow rates and concentrations to maximize the recovery of aluminium ions from water treatment residuals in a laboratory scale Donnan Dialysis cell.

2. To investigate if DD can selectively recover aluminium ions, whilst rejecting organics, and if so, by how much?

1.4 Significance of the study

The aim of this study is to assess the viability of using Donnan Dialysis for aluminium recovery within the potable water treatment process. The process presents an environmentally conscious alternative to disposing of Water Treatment Residuals in landfill sites and water bodies.

Furthermore, should Donnan Dialysis prove to be a viable alternative for efficient aluminium recovery, water treatment plants may be able to reduce their operating costs as the aluminium recovered from the Donnan Dialysis process could be recycled instead of being purchased on a regular basis.

1.5 Thesis organization

This report is arranged in four major sections, namely: literature review, experimental methodology and apparatus, results followed by conclusion and recommendations.

The literature review deals with an understanding and explanation of water treatment processes, followed by what Donnan Dialysis is, the essential equations that govern it, process limitations as well as current research and development. It is then followed by the current membrane cell configurations available and the option selected for this investigation.

The experimental methodology and apparatus is divided into two main sections. The first deals with equipment and material required for the construction of the rig, the schematic of the process, step by step instructions of the assembly of the rig, chemicals required, analytical techniques used and the experimental procedure. The second section deals with the Designs of Experiments (DOE) used as a tool for investigation in this report.

The results chapter is divided into five main sections. The preliminary runs as well as their investigation to determine if the Donnan Dialysis process is indeed feasible. It is then followed by a set of investigative runs in order to quantify the effects on the selected operating variables on the recovery and concentration of aluminium. From here a section which further optimizes the process follows. Lastly, the performance of the technology on real water treatment residuals in contrast to synthetic solutions previously used is investigated. This investigation deals with the ability/inability of the membrane to reject organics as well as how much aluminium can be recovered from real plant water treatment residuals (not synthetically made like the previous sections).

A conclusion and recommendations section follows last.

Chapter 2 Literature review

2.1 Water treatment processing

A water treatment process may be divided into three stages: primary, secondary and tertiary water treatment (Asano, 1998). The primary stage consists of screening, coagulation and flocculation. The second stage combines aeration, clarification and disinfection, lastly the tertiary stage consists of final polishes to the water such as pH adjustment. Figure 2-1 illustrates a typical water treatment unit process.

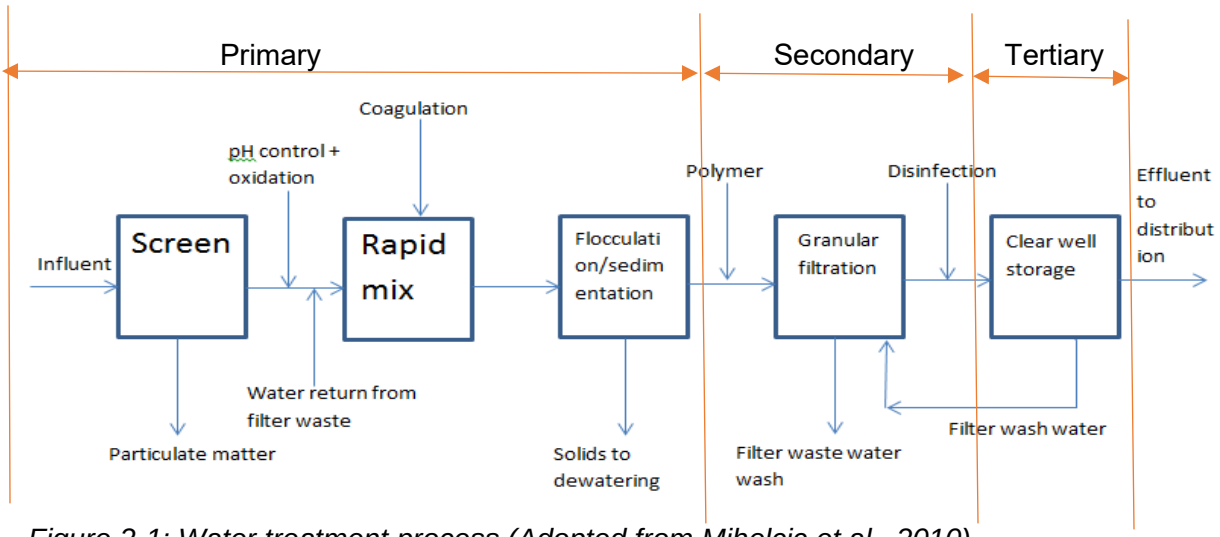


Figure 2-1: Water treatment process (Adopted from Mihelcic et al., 2010)

The focus of this project will be limited to the effluent from the primary stage of water treatment. The first stage which is screening is designed to remove floating debris and grit which may damage mechanical equipment or inhibit some biological processes from taking place (Mihelcic et al., 2010). The screening equipment of choice is usually barracks, which are parallel bars or rods of about 20-150 mm in diameter. Another alternative is the use of bar screens, these are perforated plates usually about 10 mm or less (American Water Works Association, 2003)

In order to remove dissolved organic matter and colloids once screening has taken place, a treatment combination of coagulation and flocculation is done. Coagulation is achieved by neutralizing the charges of dissolved organic matter and colloids through the use of a coagulant. A coagulant is described as a chemical which is added in order to destabilize particles and accomplish coagulation (Mihelcic et al., 2010). Figure 2-1 provides a list of some coagulant types as well as examples.

Table 2-1: Coagulants commonly used (Adopted from Mihelcic et al., 2010)

Coagulant type	Examples
Inorganic metallic coagulant	Aluminium sulphate(Alum) Sodium aluminate Aluminium chloride Ferric sulphate Ferric chloride
Pre hydrolysed metal salts	Poly aluminium chloride Poly aluminium sulphate Poly iron chloride
Organic polymers	Cationic polymers Anionic polymers
Natural plant-based materials	Moringa oleifra Opuntia spp.

After coagulation, flocculation occurs. This involves forming larger particles from the aggregation of smaller destabilized particles (Mihelcic et al., 2010). Particle stability and surface charge go hand in hand. The more stable particles are, the higher the probability that they will stay in solution.

There are five main mechanisms by which the coagulation and flocculation process occurs: Compression of the electric double layer (EDL), charge neutralization, adsorption, inter particle bridging, and lastly precipitation and enmeshment. The mechanism which applies to systems where aluminium compounds are used is precipitation and enmeshment, and thus will be the mechanism discussed.

Precipitation and enmeshment (in the context of aluminium salts)

This method generally applies to systems where aluminium or iron salts are used in high concentrations and the pH of the system is kept neutral. When high doses of aluminium or iron salts are added they form hydrous polymers that precipitate out of solution. As this precipitate forms in the system other particles become trapped in this precipitate and this results in the particulate matter settling out (Mihelcic et al., 2010).

Inorganic metallic coagulants such as aluminium sulphate (Alum) are the most commonly used type of coagulants in the treatment of water. The resulting sludge that is precipitated is discarded in landfill sites or water bodies such as rivers and lakes. While evidence linking the exposure of humans to high concentrations of aluminium by ingestion resulting in neurodegenerative diseases

has been the subject of scientific debate for decades, it has been postulated by Evuti and Lawal (2011) that the presence of aluminium salts in drinking water is a contributory factor towards the occurrence of Alzheimer's. Moreover, the aluminium salts used for water treatment are not readily available in South Africa and have to be imported from the Americas and China. The development of a technology which can recover aluminium from water treatment residuals poses to be an economic advantage for municipal potable water treatment works and as a result the country.

With this information in mind, researches sought out methods to remove as much Alum as possible from the resulting precipitated sludge, followed by recycling the Alum back into the water treatment process. Three viable routes to recover and recycle the Alum from water treatment residuals were devised: via alkalization, acid digestion and membranes (Evuti and Lawal, 2011).

Acid digestion is done with the use of sulphuric acid, the aluminium hydroxide in the precipitated sludge is reacted with the sulfuric acid in order to reform Alum according to the following equation:

$$2Al(OH)_3 3H_2O + 3H_2SO_4 + 2H_2O \rightarrow Al_2(SO)_4 14H_2O \qquad \text{Equation 2-1}$$

The process is carried out a pH between 1 and 3 where an aluminium recovery between 70 and 80% is achieved. While this process is both low cost and highly efficient, it has a major drawback. The recovery of Alum is a non-selective process, this means that in addition to Alum being recovered, other soluble metals as well a large number of humics and aromatic organics are also recovered in the process. The problem with this is that when the Alum gets recycled into the water treatment process, it does so with these other metals and undesired organics, this results in an unwanted build-up in the process over time (Evuti and Lawal, 2011).

Due to aluminiums amphoteric nature it can also be recovered under alkali conditions. A recovery of 80% was found to be possible under alkali conditions at a pH range of 11 to 12 by Evuti and Lawal (2011). A ratio of 3:7 of sodium hydroxide to lime was used for the reaction. The drawbacks of alkalization are similar to those of acidification described above.

Lastly, the third processing route involves the use of membranes. There are a variety of membrane types which are suited for different industrial applications. These range from Ultrafiltration membranes to Reverse Osmosis membranes. Cheng et al. (2016) investigated the specific use of Ultrafiltration and Nanofiltration membranes in concentrating and recovering leached aluminium from acidified water treatment residuals. They found two major drawbacks with this separation technique. While aluminium ions could be rejected (14% rejection for Ultrafilters and 96% for Nanofilters) the membranes were found to be non-selective. Organics were found to be concentrated as well. In addition to this, the membrane operating pressures were found to increase in the system as a result of fouling from organics on the membranes surface. Baker (2013) also expressed that the disadvantage of separation techniques which exploited size in order to achieve separation was their high energy requirements which resulted as a consequence of the operation being pressure driven.

Due to the lack of readily available technology which could provide high selective recovery of aluminium ions from water treatment residuals, a relatively new technology called Donnan Dialysis was explored. It is discussed in section 2.2

2.2 Donnan Dialysis

Donnan Dialysis is a membrane process. It utilizes the counter diffusion of ions through an ion exchange membrane. The process is driven by an electrochemical potential gradient across the membrane (Prakash et al., 2004). The process is performed counter currently with the objective of taking dilute solutions and concentrating them into a small volume.

There are two types of membranes processes available for Donnan Dialysis. The first is cationic exchange and the second is anionic exchange (Davis, 2001) in both processes a membrane separates two compartments containing two different electrolytic solutions. The cationic membrane is essentially a polymer with fixed negative charges dispersed uniformly within the film. The counter ions which are positively charged are free to exchange with other positively charged ions from the solutions in both compartments, while the negative counterparts of the positive ions in solutions are not able to interact with the membrane due to their charge (Davis, 2001).

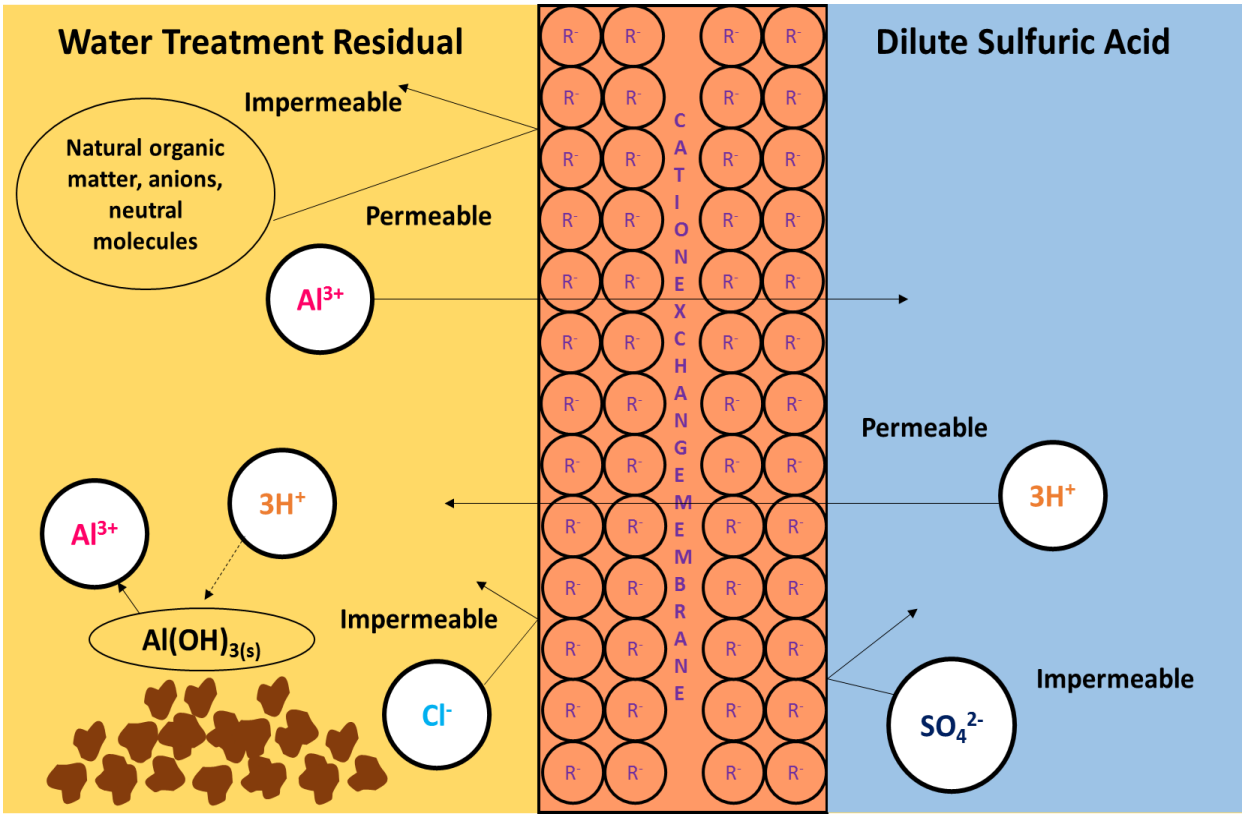


Figure 2-2: Donnan Dialysis process and the transfer of ions through cation exchange membrane (Adapted from Sarkar et al., 2010)

Figure 2-2 illustrates the cationic exchange process. Two compartments are separated by a cationic exchange membrane. The side which contains water treatment residuals is termed the feed side. The other compartment which contains acid is named the sweep side. Only positive ions such as hydrogen and aluminium are permitted through the membrane, negative ions and organic matter is unable to permeate the membrane. Initially the feed side only contains water treatment residuals and the sweep side sulphuric acid. The ionic exchange of hydrogen ions to the feed side and aluminium ions to the sweep side is a function of time, the feed and sweep are

continuously recycled. This ionic exchange continues until equilibrium is reached, aluminium ions which are now concentrated in the sweep side are then recovered.

The anionic membrane operates under the same principle as the cationic membrane, with the primary difference that positive charges are fixed in the membrane and the counter ions are negatively charged. The membrane only interacts with negative ions in both compartments and hence would not work for the recovery of aluminium ions (Davis, 2001).

2.2.1 Essential equations for Donnan Dialysis

There are two essential equations that are crucial to the Donnan membrane process. The first is the Nernst-Planck equation (Equation 2-2) which is used to describe the amount of permeate produced per unit area of membrane surface per unit time, also known as the membrane flux.. Through Equation 2-2, the rate of transport of ions through the membrane can be determined. It can be seen that the higher the initial concentration and ionic charge are, the faster the rate of transport of ions across the membrane will be.

The following five assumptions are made in order to derive the Nernst-Planck equation (Ho et al. 1993);

- The transport is controlled by membrane diffusion.
- The amount of anions in the membrane is negligible compared with its ion exchange capacity. No anions can also permeate the membrane
- Thermodynamic equilibrium exists at the membrane-solution interface.
- Osmotic water flow across the membrane can be ignored.
- The overall electro neutrality is preserved in the system.

With these assumptions in mind, the Nernst- Planck equation may be written as:

$$J_m = -D_m\left(\frac{dC_m}{dl} + \mathrm{Z}_i C_m \frac{F}{RT}\frac{d\emptyset}{dl}\right) \qquad \text{Equation 2-2}$$

Where J_m is the flux;

C_m is the metal ion concentrations in the bulk solution,

D_m is the diffusivity,

l is the thickness of the membrane,

R Is the gas law constant,

T is the absolute temperature,

Z is the ionic charge,

F is Faradays constant and θ is the electric potential.

The second essential equation provides a way to understand the relationship between the initial concentration, and final solution concentration of both the feed and sweep side and is provided by Davis (2001) as follows:

$$\left(\frac{[Ca]^+{}_1}{[Ca]^+{}_2}\right)^{\frac{1}{Za}} = \left(\frac{[Cb]^+{}_1}{[Cb]^+{}_2}\right)^{\frac{1}{Zb}} \qquad \text{Equation 2-3}$$

The subscript 1 denotes the ions in the feed compartment and 2 denote the ions in the sweep side compartment. C_a And Z_a are the concentrations and ionic charge of the target metal. C_b And $Z_b$is the concentration and ionic charge of the species substituting the target metal. The implications of this equation are as follows:

- A high initial concentration of the substitute ion results in a high final concentration of the target metal ion.
- The higher the ionic charge of the target metal to be recovered and the lower the ionic charge of its substitute ion are, the higher the recovery and final concentration of the target metal will be.

2.2.2 Process limitations inherent to Donnan Dialysis

2.2.2.1 Concentration polarization

A major factor that influences the flux in Donnan Dialysis exchange membranes and consequently their performance, is a phenomenon known as concentration polarization (Amang et al., 2003). It is illustrated in Figure 2-3.

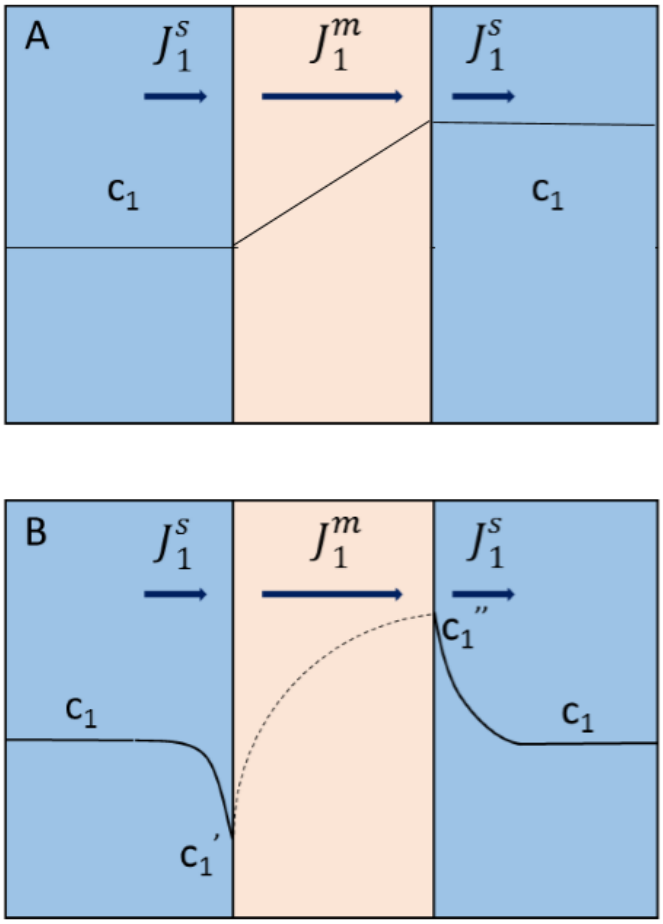


Figure 2-3: Ideal (A) and non-ideal (B) concentration polarization scenarios that affect membrane processes (Adapted from Bhuttacharjee, 2017)

Concentration polarization is when a gradient occurs at the membrane and solution interface due to the selective transport of certain species faster than others. Polarization is generally known to occur when a significant boundary layer exists on the membrane surface (Baker, 2013). The concentration of the more selectively transported species is higher in the bulk phase, as it approaches the membrane interface and enters the boundary layer, the concentration decreases.

The concentration gradient then increases across the membrane due to the rate of permeation of target species through the membrane. On the other side of the membrane the concentration then decreases with increasing distance from the membrane. Part A of Figure 2-3 provides an illustration of an idealistic scenario (system with no concentration polarization), while part B of Figure 2-3 illustrates a scenario with concentration polarization (Bhuttacharjee, 2017).

According to Baker (2013), concentration polarization in a membrane system can be reduced by promoting turbulent flow in the system. The objective of the turbulent flow is to reduce the boundary layer thickness by promoting uniform species concentration throughout the vessel. A state of turbulence can be achieved via two methods. The first one is by increasing the velocity of the flow over the membrane. The second method would be by manipulating the flow patterns of the solution with the aim of trying to produce a turbulent regime. Sheet or mesh spacers as well as baffles can be used to achieve this (Baker, 2013).

2.2.2.2 Osmosis

Osmosis is the transport of molecules through a semipermeable membrane from a region of low concentration to a more concentrated area. Over the years, several milestones in terms of studies towards the understanding of water transport characteristics of Nafion (a type of cation exchange membrane) membranes have been achieved. These studies are briefly discussed in this section.

The first study was conducted by Okada et al. in 1998. It was found that the number of moles of water transported across a Nafion 117 membrane is attributed to two main effects, namely, the electrostatic interactions between ions in solution and water dipoles as well as an effect due to the size of the cation present in solution. Okada et al.(1998) observed that for hydrophilic cations, the transfer of water across a membrane increased as ionic radius of the cation decreased. For hydrophobic cations however, the transfer of water across the membrane increased with ionic radius. Electrostatic interactions in solution were found to aid the transport of water when dipole charges between cations and water molecules were dominant. The cations were found to attract water molecules around them and were seen to move in unison with those water molecules. Lastly, from experimentation the group observed that larger cations tended to also aid in the transport of water molecules by “pushing” water through membrane channels by volume exclusion.

Duan, Wang and Benziger (2011) built on the research of Eikerling et al.(1998) who hypothesized that water transport across Nafion membranes was due to driving forces such as capillary, pressure, osmotic pressure and an external pressure gradient. Duan et al. (2011) published their research and findings in 2011. The group experimentally investigated the effect of temperature and pressure on the flux of water through Nafion membranes. They found that the transport of water across the membrane increased with temperature and pressure. As the temperature was increased the viscosity of water decreased and the hydrophilic volume fraction increased and hence the increase in water transport across the membrane with temperature. In terms of pressure, the research is unclear as to what the reason for the increase in water flux across the membrane with pressure is.

Lastly, Prakash et al. (2004) further worked on research which utilized Nafion membranes. The objective of the research was to concentrate aluminium using Donnan Dialysis. Prakesk et al. (2004) demonstrated that the graph for the concentrating of aluminium ions using Donnan Dialysis could be divided into three main regions, this is illustrated in Figure 2-4.

The first zone, which is zone A, displays a linear trend and is governed by a high electrochemical potential and is termed the “kinetically driven zone”. As the concentration of aluminium decreases in the feed side and the electrochemical potential decreases, the rate of recovery of aluminium decreases. This can be seen by the decrease in the gradient, this is zone B and is termed the

Donnan equilibrium zone. Lastly, when the aluminium recovered reaches a maximum it is seen to decrease again. This is Zone C and is predominantly characterized by hydrodynamic effects. Prakash et al. (2004) hypothesized that the water transport was due to osmosis and termed the zone as the “osmosis driven” zone. The transport effects of water become more visible here and the end result is a reduction in the concentration of aluminium due to water dilution.

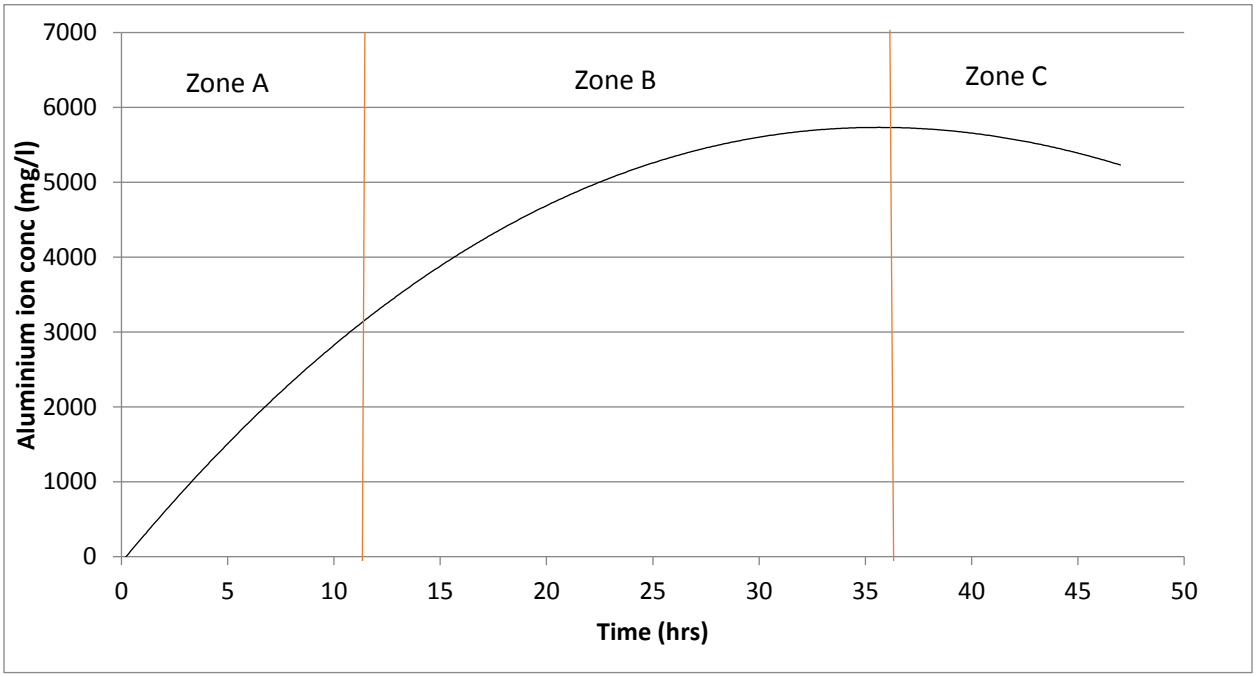


Figure 2-4: Aluminium ion concentration and postulated three zones it can be divided into (Adapted from M. Van Rooyen, 2012)

2.3 Current status research and development of Donnan Dialysis

Donnan dialysis has uses both in the mineral processing industry as well as the water treatment industry. Below are cited examples of the uses of the Donnan Membrane Process in laboratory scale experiments.

Table 2-2: Case studies of Donnan Dialysis technology applications

Researchers	Description of process	Motivation
Prakash et al. (2004)	A method was formulated to selectively recover coagulants such as Alum from water treatment residuals using the Donnan Membrane Process. The process was found to selectively recover about 70% Alum under the following conditions; - 6.6 litres of water treatment residuals on feed side. - 1.5 litres of 10% sulphuric acid on sweep side. - pH between 3-3.5 - Nafion 117 membrane - Duration of experiment was 24hrs	The motivation behind the recovery of Alum was to mitigate the improper disposal of Alum in landfill sites or water bodies because of its hazardous nature.

Prakash and SenGupta (2003)	Two membranes, a homogeneous Nafion 117 and a heterogeneous Ionca 3470 were studied for recovery. An 80% selective concentration of Alum was achieved for the homogeneous membrane under the following operating conditions: - 3 litres of water treatment residuals on the feed side. - 1 litre of 1 M sulphuric acid on the sweep side - Duration of experiments ranged from 9-24 hours	To assess the impact of different membrane morphology on recovery with respect to kinetics, perm selectivity, osmotic and fouling effects and quality of Alum yield. It was found that the homogeneous membrane had a 50% higher recovery than the heterogeneous membrane. Secondly the heterogeneous membrane was found to not have any osmosis effects unlike the homogeneous membrane. Lastly, the interdiffusion coefficient of the homogeneous membrane was found to be an order of a magnitude larger than the heterogeneous membrane.
Marzouk et al. (2013)	The removal of chromium (VI) from industrial waste water resulting from processes such as electroplating, dies and textiles was investigated. It was investigated under the following conditions: - Cr(VI) concentration of 1 g/l - At a pH of 4 - Using two anion exchange membranes, namely; Selemion AMV and Neosepta AFN. - A NaCl concentration of 0.1M in sweep side.	The removal of chromium in waste streams was found to be essential due to chromium's detrimental impact on ecosystems and public health.

Cengeloglu et al.(2003)	The recovery of titanium, iron, aluminium and sodium from red mud found at aluminium plants using a cationic exchange membrane under the following conditions: • A 40 ml feed and sweep compartment volume • The feed compartment was red mud diluted in a 50% aqueous solution • The sweep side was HCl ranging in concentrations of 0.05M-1M • Three ionic exchange membranes were investigated: ICE-450,Neosepta CMX and Neosepta CMB	The objective was to recover valuable metals from disposed waste streams
Akretche and Kerdjoudj (2000)	The efficiency of separating gold, silver and copper cyanide complexes was determined using Donnan dialysis. It was investigated under the following conditions: • A feed solution of 250 cubic centimetres. • A sweep solution of 250 cubic centimetres. • NaOH of 6M used as stripping solution. • Experiments performed for single ion metal component in presence of 0.2 M KCN at pH of 9.	The motivation for this was the potential of recycling reactants and thus making the process more cost efficient. An additional consideration was the harm that cyanide compounds do to the environment.

Hichour et al. (1999)	The removal of fluoride in drinking waters with the use of Donnan Dialysis with an ionic exchange membrane was studied under the following conditions; - A feed volume of 21.12 cubic centimetres. - A sweep side volume of 410ml. - NaCl in the sweep side at a concentration of 10 moles per litre. - pH of 5	The objective was to reduce the fluoride content in water to make it suitable for human consumption.
Wisniewski et al. (2006)	The denitrification, defluorination and removal of bicarbonates using Donnan Dialysis under the following conditions: - Feed volume ranging from 20.5-10 litres - Feed concentration of 5mM - NaCl as the sweep side solution - Membranes used were: Selemion AMV,Selemion DMV, Neosepta AFN, Neosepta AMX.	To reduce the scaling effects caused by anions during electrodialysis.

Hamouda et al.(2017)	The removal of nitrates using Donnan Dialysis was studied under the following conditions: • Feed and sweep volumes of 25ml • Sweep side of NaCl at concentration ranges of 0.001-0.1M	The objective was to reduce nitrate concentrations in water to acceptable thresholds.
Zhao et al. (2010)	The removal of arsenate from ground water utilizing Donnan Dialysis under the following conditions: • Feed concentrations of 250-540 micro grams per litre. • Sweep side of NaCl at a concentration of 12 grams per litre. • A total treatment capacity of 35 litres. • Experimental duration of 24 hours and aeration at 4.7 litres per minute.	To remove up to 80%of arsenate found in ground water and raw streams in order to mitigate the environmental and health issues associated with arsenic.
Agarwal et al. (2016)	The separation efficiency of Donnan Dialysis for the selective removal of gold from complexes with copper and nickel in aqua regia under the following conditions: • A feed solution of 100 ml • Sweep concentration of 0.5m NaCl • Micro pore grafted poly propylene membrane was used.	To determine if gold could selectively be removed from copper and nickel complexes. 97% of gold was selectively recovered from a feed containing a 1:500 Au:Cu solution.

Despite the process limitations which were found to affect the Donnan Dialysis process in section 2.2.2 such as osmosis and concentration polarization, the authors discussed in Table 2-2 demonstrated the use of Donnan Dialysis in various applications. From studying the various operating conditions and recoveries in the applications above, one can deduce that the selectivity and transport of ions across a membrane depend on the following factors:

1. Feed concentration
2. Concentration of electrolytic solution (sweep concentration)
3. Membrane type and morphology
4. Electrolytic chemical used in the sweep side
5. Experimental duration
6. Valence of target ion
7. Flow rates and turbulence of the feed and sweep side streams

The seven factors fall into three main categories, namely:

1. Factors which have been extensively investigated and for which sufficient Donnan Dialysis information exists from literature to make proper selection of operating conditions.

2. Factors which have been investigated and for which theory exists, but practical findings are less extensively documented.

3. Factors for which limited or no information exists in regard to the effect of the factor on the Donnan Dialysis process, and where extensive future investigation is required.

These three groups are discussed in sections 2.3.1, 2.3.2 and 2.3.3.

2.3.1 Donnan Dialysis factors which have been extensively investigated

The two factors which have been extensively investigated in literature are:

1. Valence of target ion

2. Membrane type and morphology

In terms of the effect of the valence of the target ion, authors Miyoshi (1997) as well as Xue et al. (1991) investigated the effect of having different valance ions on the feed and sweep side of the Donnan Dialysis cell membrane. They found experimentally that in general, monovalent (those with an ionic charge of one) driving ions (in sweep side) paired with higher valence (valence greater than one) feed ions had a larger driving force than equally charged feed and sweep side ions. They also discovered that feed and sweep side ions with equal valences had a larger driving force than a feed side solution with ions having lower valences than the sweep side. This can also be deduced from the Donnan equilibrium equating charges and concentrations provided by Davis (2001).

Miyoshi (1997) hypothesized that the reason for this was that monovalent ions were free to move from one fixed ion to near another fixed ion, however bivalent/trivalent ions needed to migrate from two/three fixed ions to another two/three, which was found to be much more difficult to achieve. Table E-1 in Appendix E provides the species in the feed and sweep sides as well as their respective initial concentrations for the 26 runs Miyoshi (1997) performed to establish this.

Keeley et al. (2014) investigated the effect of membrane type and morphology on the Donnan Dialysis process. They found that homogeneous sulfonated membranes demonstrated diffusion rates 5 to 10 times higher that their heterogeneous counterparts. Moreover, they were found to be 30 times more selective for aluminium. Prakash and Sengupta (2003) attributed this to the extreme hydrophobic nature and even distribution of the sulfonate groups found in the homogeneous membranes.

Keeley et al. (2014) investigated the performance in terms of flux of four different cationic exchange membrane to determine which one had the best overall performance. The results are displayed in Table 2-3.

Table 2-3: Membrane types and performance

Membrane type	Functionality	Flux over 4 hrs with 1 M sulphuric acid sweep($eq.m^{-2}\cdot s^{-1}$)	Ion	References
Dupont Nafion 117	Homogeneous sulfonated	8.27×10^{-4}	Al^{3+}	Prakash and Sengupta (2003)
Dupont Nafion 117	Homogeneous sulfonated	2.13×10^{-4}	Fe^{3+}	Prakash and Sengupta (2003)
Dupont Nafion 117	Homogeneous sulfonated	$8.4\times*10^{-4}$	Al^{3+}	Prakash et al. (2004)
Sybron Chemicals Ionac MC 3470	Heterogeneous sulfonated	7.34×10^{-5}	Al^{3+}	Prakash et al. (2004)
Gelman Sciences ICE-450 SA3S	Homogeneous sulfonated	2.25×10^{-5}	Cr^{3+}	Tor et al. (2004)
Gelman Sciences ICE-450 SA3T	Heterogeneous sulfonated	2.07×10^{-5}	Cr^{3+}	Tor et al. (2004)

Table 2-4 illustrates that for trivalent ions, Dupont Nafion 117 membranes provide the highest fluxes from the feed to the sweep and thus provided the highest recoveries.

2.3.1.1 Nafion 117 cationic exchange membrane

The cationic exchange membrane that was used was a Nafion 117 membrane manufactured by Dupont industries. The 117 denotes that the nominal thickness of the membrane is 183 micron. This specific membrane has an equivalent weight of 1100. The equivalent weight is a relation between two important parameters which determine the membranes ability to conduct and transport ions, it is the mass of dry membrane per mole of sulfonic acid groups (Napoli et al., 2013). The structure of the membrane is as follows: Perflourinated polymer backbone which has sulfonic acid groups branching off of it. The sulfonic acid group is then surrounded by a hydrophobic matrix of a tetrafluoroethylene support and perfluorovinyl ether pendant side chains. The membrane provides the transport of protons through water sorption. The water sorption increases the size of the hydrophilic domains present, this then provides the necessary channels

for ionic transport to occur (Napoli et al., 2013). The formula for the structure of the membrane is provided in Figure 2-5 for ease of reference. It is also important to understand that the perfluorinated polymer backbone is responsible for the membranes stability and ability to operate over a wide operating range. From pH levels of 1 to 14 and temperatures ranging from 5 to 130 °C.

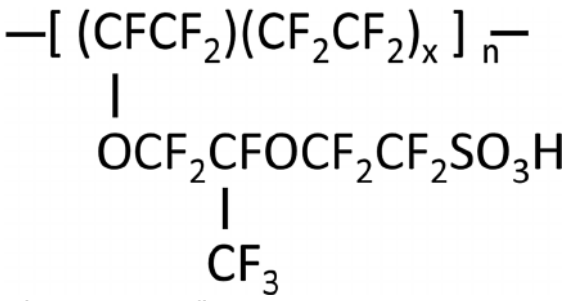


Figure 2-5: Nafion structure

2.3.1.2 Activation of the membrane

Membrane activation is an essential part of Donnan Dialysis, without this step very little hydration of the tortuous pathways is achieved and thus very little ionic transport will be observed. Although there are different schools of thought on how to perform membrane hydration by researchers such as Duane et al. (2011) and Napoli et al. (2013), the common thread is that all these researchers agree that membrane conditioning through aqueous acid immersion is of the utmost importance.

Napoli et al. (2013) proposed that before a new membrane is used for the first time, it is crucial to ensure that all the impurities and factory defects are removed from the surface of the membrane. This is done by conditioning the membrane in a 3% HCl warm solution at an elevated temperature of about 90℃. This is done for an hour, where after the membrane is then removed and rinsed off with deionized water for about 15min.

After this step, research by Napoli et al. (2013) has shown that further immersion of the membrane in a dilute (1% HCl) solution for 3 hours further increases the inter-pore hydration of the membrane which in turn further increases ionic transport.

2.3.2 Donnan Dialysis factors which have been partially or only theoretically investigated

The four factors below have been investigated in theory by Davis (2001), Prakash (2004) and Ho et al. (1993):

1. Feed concentration
2. Sweep Concentration
3. Feed volume
4. Sweep volume

Davis (2001), Prakash (2004) and Ho et al. (1993) used mathematical equations to relate the initial concentration and volumes of the feed side to the final volumes and concentrations of the feed and sweep sides. Equations 2 and 3 in section 2.2.1 shown and discuss this.

Prakash (2004) as well as Prakash and Sengupta (2003) performed laboratory experiments to investigate the feasibility of recovering aluminium sulphate from Water Treatment Residuals. While they were successful in recovering up to 80% of the aluminium sulphate, their investigations did not establish the effect of varying both the initial feed and sweep concentrations and their treatment combinations on the final aluminium sulphate recovered.

2.3.3 Donnan Dialysis factors with limited or no information

Limited or otherwise generic information is known about the below factors as regards their effect on the recovery of Alum in the Donnan Dialysis process:

1. Flow rates and turbulence of the feed and sweep streams
2. Electrolytic chemical used in the sweep stream
3. Experimental duration

Baker (2013) and Amang et al. (2004) found concentration polarisation to be a process limitation inherent to Donnan Dialysis. They hypothesized that by promoting turbulence through increased fluid velocity in the dialysis process, the effect of concentration polarisation could be reduced .This was discussed in detail in section 2.2.3. Their research did not examine the effects of varying the flow rates of the feed and sweep sides, their treatment combinations and their effect on concentration polarisation and ultimately the final recovery of aluminium sulphate.

Various researchers documented in Table 2-2 of section 2.3 have investigated Donnan Dialysis with the objective of recovering various target ions using different sweep ions as the driving force. However, none investigated the effect of different driving ions in the sweep and their effect on recovering aluminium ions from Water Treatment Residuals. The work of Okada et al. (1998), Duan, Wang and Benziger (2012) and Eikerling et al. (1998) pointed out that water was transported across Nation 117 membranes through various mechanisms of which one was found to be osmosis. They hypothesized that ions of different sizes, osmotic pressure and valence affected the amount of water transported across the membrane from the feed side to the sweep side differently. This water transport in turn affected the final sweep side concentration that could be achieved. Ideally, no water transport would be optimal. Van Rooyen (2012) and Prakash (2004) investigated this water transport phenomenon on the recovery of aluminium ions from Water Treatment Residuals utilizing a Nafion 117 membrane. They found that water transport using sulphuric acid in the sweep as the driving force did indeed occur. They did not however investigate the possibility of using another acid in the sweep side as the driving force in order to minimize water transport across the membrane.

Lastly, the exact experimental duration in order to obtain the highest recovery and concentration of target ions for Donnan Dialysis is not known. It has been postulated by Zhao et al. (2010), Prakash (2004), Van Rooyen (2012), Prakash and Sengupta (2003) to be between 20 and 30hrs and to rely heavily on the operating conditions chosen. Of the four groups of researchers above, Prakash (2004), Van Rooyen (2012) and Prakash and Sengupta (2003) specifically looked at the recovery of aluminium ions using Donnan Dialysis while Zhao et al. (2010) focused on the recovery of arsenate. Their operating conditions can be found in Table 2-2.

2.4 Viable Donnan Dialysis membrane configurations

This section discusses the ideal design criteria for an industrial membrane, the performance characteristics of various module types as well as some successful Donnan Dialysis cell designs which have been reported in literature.

2.4.1 Desired criteria for Donnan Dialysis membrane module design

The main design criteria as cited by Davis (2001) for a Donnan Dialysis membrane module are that:

1.) The membrane module should promote high cross flow velocities at low flow rates in order to minimize fouling and boundary layers.

2.) The module should have a high area to volume packing ratio.

3.) High resistance to thermal attack.

4.) High resistance to chemical attack.

5.) The membrane and module should not require extensive pretreatment of the raw feed.

6.) Should be scalable in order to accommodate larger throughputs in future if necessary.

The Donnan Dialysis membrane modules which have been reported in literature to successfully work have been displayed in Table 2-4

Table 2-4: Donnan Dialysis cell design reported in literature

Researchers	Description of process	Setup
Wallace.R,W (1967)	To concentrate uranyl ions from dilute solutions of uranyl nitrate.	Plate and frame with membrane sandwiched between
Marzouk et al. (2013)	The removal of chromium from industrial waste water.	Two compartment cell (Flat sheet)
Akretche and Kerdjoudj (2000)	The efficiency of separating gold, silver and copper cyanide complexes using DD.	Three compartment cell (Flat sheet)
Pozniak and Trochimizuk(1990)	Producing sodium chloride from sodium hydroxide and hydrochloric acid.	Tubular membrane
Wodzki et al. (1995)	Recovery of metals from electroplating waste solutions and sludge .	Three compartment cell (Flat sheet)

Table 2-4 illustrates the two main successful module designs applicable for industrial use with regard to Donnan Dialysis. Namely, tubular modules as well as plate and frame modules (the two and three compartment cell are a variation of the plate and frame). Based on the required design criteria discussed in section 2.4.1 each membrane module is investigated in section 2.4.2 and 2.4.3. In these sections, the major advantages and disadvantages of the modules are discussed. This is followed by a summary of the performance characteristics of the membrane in section 2.4.4.

2.4.2 Plate and frame modules

This design is one of the earliest in the membrane industry. The plate and frame design comprises of a membrane and at times a spacer sandwiched between two blocks/plates (Baker, 2013). The module may be seen in Figure 2-6. The diagram on the left hand side shows the flow of fluid along the membrane and spacer before the membrane has been sandwiched in between the plates. The right hand side diagram illustrates the complete module once it has been fitted with plates.

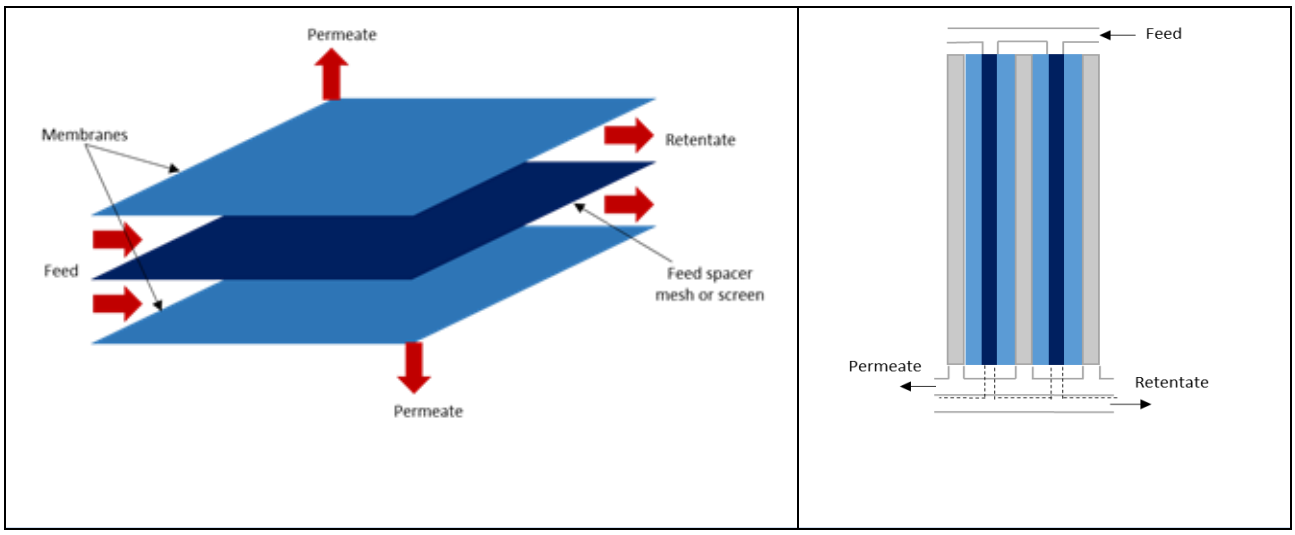


Figure 2-6: Plate and frame module schematic (Adapted from Baker, 2013)

Essentially the module works by having a feed inlet stream into one of the blocks/plates, the feed stream is then forced across the surface of the sandwiched membrane. From here, there are two output streams, one a permeate stream and the other a retentate stream.
The advantages of this module are:

- They are relatively easy to assemble.
- Membranes can easily be replaced if there is a problem with them.
- Equipment errors such as leakages are easy to spot.
- The plate and frame modules are easily scalable and can be packed together in parallel to support large industrial scale applications.

The major disadvantage of the plate and frame module is the low membrane area per volume.

2.4.3 Tubular modules

Tubular modules consist of a large tube which contains smaller tubular compartments inside it. These smaller compartments are each fitted with a membrane. Figure 2-7 provides an illustration of tubular modules.

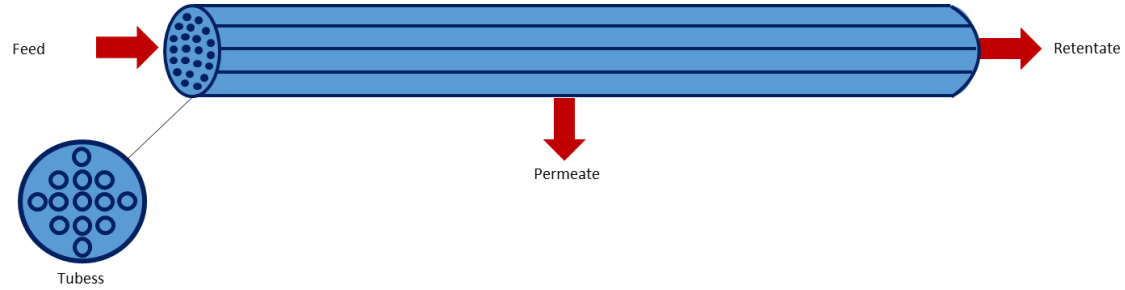


Figure 2-7: Tubular module schematic (Adapted from Baker, 2013)

The feed is pumped parallel to the large tube into the smaller compartments; it then is transported through the membranes. The retentate flows out of the opposite end of the tubes, while the permeate flows out perpendicularly to the tubes.

Some advantages of tubular modules are as follows (Baker, 2013):

- They are easy to clean.
- Have a high resistance to fouling.

The two main setbacks of these modules are that:

- They are relatively expensive.
- They have a low packing density.

2.4.4: Module performance characteristics summary and cell designs reported in literature

Table 2-5 provides a summary of the performance characteristics of the membrane modules discussed above.

Table 2-5: Performance characteristics of various membrane types

Module Type	Promotion of high cross flow velocity	Area to volume packing ratio	Amount of pre-treatment required
Flat sheet (plate and frame)	Low	Low	Low
Tubular	Medium	Medium	Medium

2.5 Limitations towards full-scale operation, and current R&D to overcome those limitations

There is common consensus amongst researchers so far on two current limitations of the Donnan membrane process. The first limitation of this process is the extremely slow kinetics of ion transport across the dialysis membrane and the time taken for equilibrium to be achieved. This factor makes it undesirable to make Donnan Dialysis an industrial application because the concentration and separation of metals and other ions takes too long to occur (Akretche, 2000). A solution to this was proposed by Akretche (2000) which was to in-corporate Donnan Dialysis in other separation technology treatment circuits and not just as a stand-alone system. They suggested two possible methods.

The first method was to combine Donnan dialysis with electro dialysis. The objective of Donnan Dialysis would be to remove some of the multivalent ions from the electro dialysis feed in order to be able to increase the limiting current density in the electro dialysis cell. Doing so would result in a higher flux and thus increase the kinetics of the separation process. The second option involved using the Donnan membrane process as a hybrid process with Reverse Osmosis. Conventionally Reverse Osmosis recovery is limited by scaling on the membrane surface. Using Donnan Dialysis as a pre-treatment step would reduce the amount of scaling on the Reverse Osmosis membrane, increase the process recovery and have faster kinetics than if only the Donnan membrane process was used.

The second deterring factor of using Donnan Dialysis as pointed out by Hamouda (2017) is the high purchasing cost of the membranes. Hamouda (2017) pointed out that this phenomenon was not new, and like all emerging technologies initially the cost of purchase will be expensive.

2.5.2 Summary

Ionic exchange membranes and Donnan Dialysis are relatively new with commercial application being achieved in the last 50 years. While the technology is yet to be fully researched and its full potential not yet understood, the common consensus amongst researchers is that its unique advantage of not being pressure driven and thus not having high energy requirements or being susceptible to fouling possess as a huge advantage to its traditional membrane counterparts such as Micro and Nano filtration.

More specifically, in terms of recovering aluminium ions from WTRs, Donnan Dialysis' ability to selectively recover aluminium while simultaneously rejecting organics puts it neck and shoulders above other approaches of recovering aluminium from WTRs such as alkalization and acidification.

The major drawbacks with Donnan Dialysis have been cited to be its long operation time to recover ions as well as the large capital costs involved in purchasing the ion exchange membranes.

Current solutions to minimise these drawbacks involve using the technology in tandem with others such as electro dialysis in order to reduce the time required to achieve the desired recoveries.

Chapter 3 Experimental methodology and apparatus

3.1 Introduction

This chapter focuses on the apparatus used for the Donnan Dialysis investigation. A detailed description of the apparatus is provided in the form of a process schematic, a drawing with manufacturing dimensions of the cell used, as well as an illustration of the experimental setup.

The chemicals used, their descriptions as well as the analytical techniques used in the investigation are discussed next in sections 3.5 and 3.8.

Lastly, the projects experimental design is divided into three main parts. The first part consists of the design of experiments for the scanning runs which were performed at both high feed and sweep concentrations. For this part, a full factorial design of experiments has be used.

The second phase consists of further experimentation with the use of the Box Behnken design. The objective of this section was to further modify and optimize the process from the information and shortcomings observed in the first section of experimentation.

The last design of experiments used was for the equipment validation section. For this section a randomized complete block design was used to calibrate the pumps used. In addition to this, some guidelines on addressing leakages in the system are provided.

3.2 Donnan Dialysis process schematic

Upon careful consideration of the advantages and disadvantages of the modules discussed in the literature section and comparing them with the required criteria for apparatus, it was concluded that the Flat sheet setup will be modified and is best suited for this project as it meets most of the specified needs. Figure 3-1 provides the schematic for the apparatus used.

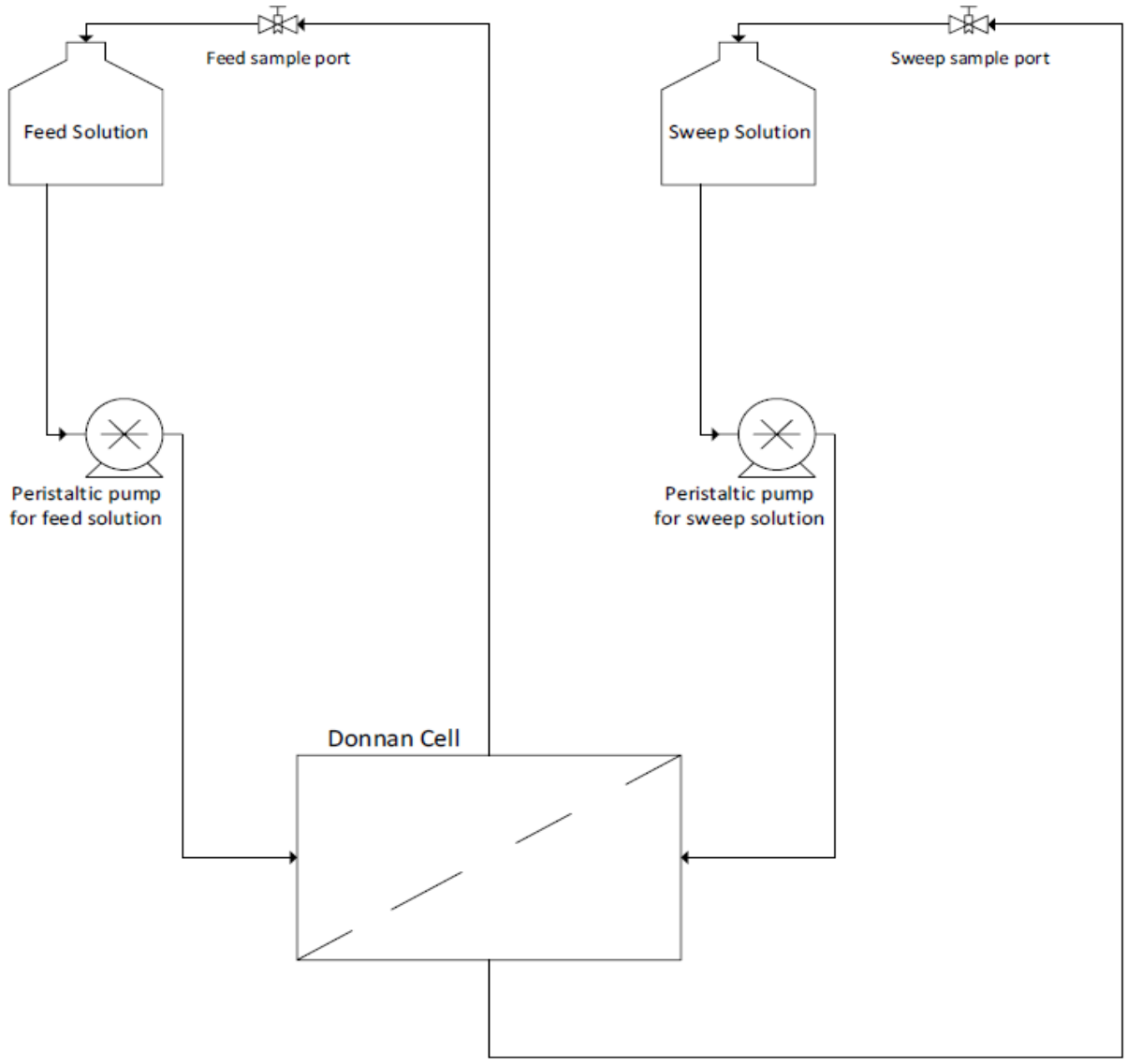


Figure 3-1: Schematic of Donnan Dialysis experimental setup

3.3 Process description for Donnan Dialysis experimental rig

Water treatment Residuals/synthetic Alum from the feed tank were pumped using a peristaltic pump. The inner tubing of the peristaltic pump was PTFE tubing with and ID of 6mm. The feed was pumped to a Nafion 117 cationic exchange membrane manufactured by Dupont industries with a nominal thickness of 183 micron. The tubing used was also PTFE with an ID of 12mm. Similarly, hydrochloric acid was pumped from the sweep tank using a peristaltic pump and the same tubing to the Nafion 117 membrane. The acid stream contacted the membrane on the opposite side to the Water Treatment residuals feed stream to allow for ion exchange to occur. The experiment was conducted for 48 hours with both the feed and sweep sides in recirculating mode. Both the feed and sweep tanks were agitated with magnetic stirrers. An illustration of the experimental laboratory rig used may be seen in Figure 3-2.

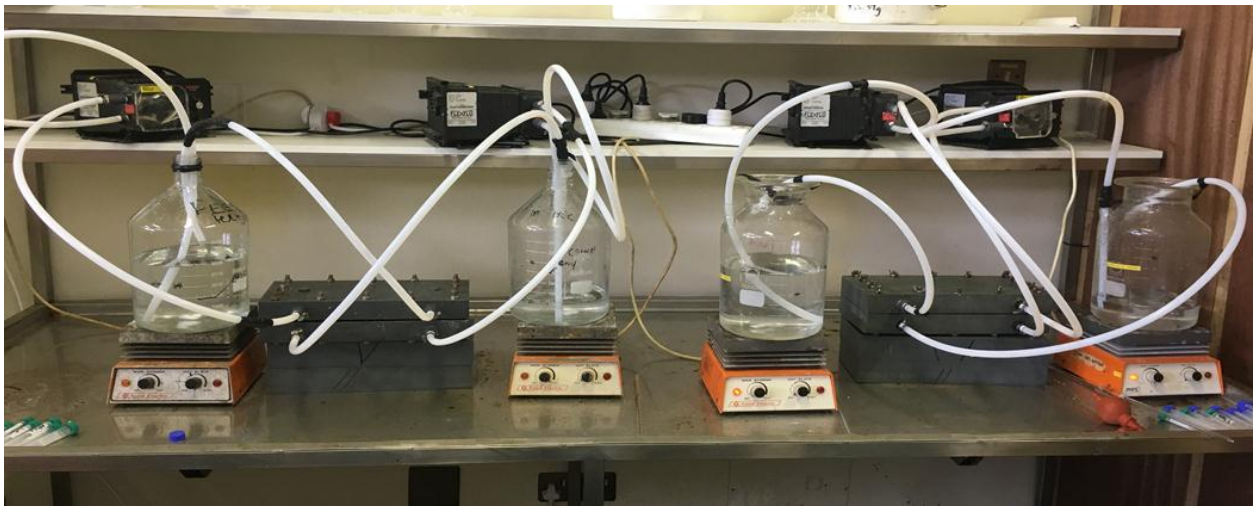


Figure 3-2: Donnan Dialysis experimental rig

The specifications and dimensions for designing each cell the Nafion membranes are housed in are illustrated in Figure 3-3. The Reynolds number was determined for the geometry depicted in Figure 3-3 utilising calculations for flow over a flat plate. The Reynolds number for the flow rate range investigated were found to range from 9400 to 23600, where the transition between laminar and turbulent flow begins at a Reynolds number of 500,000 for flow over a flat plate. The results indicate that flow over the membrane is laminar and concentration polarization effects in the system may be significant. The working volume of the cell on either side of the membrane is 75cm^3 .Working volumes from previous research conducted by Prakash et al. (2004) were unavailable in their publications for comparison.

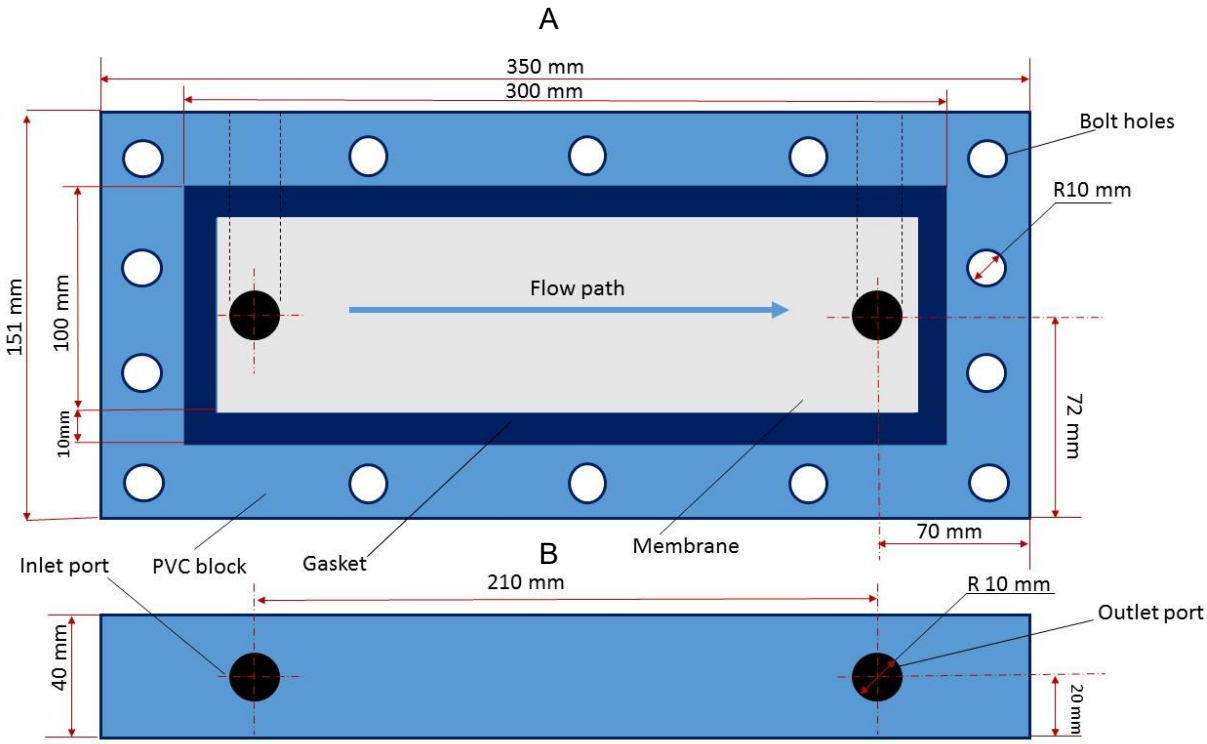


Figure 3-3: Design and dimensions of DD cell

Figure 3-3 A depicts the top view of the Donnan Dialysis cell and Figure 3-3 B depicts the side view. The length, width and height of each half of the PVC blocks encasing the cationic exchange membrane were 350 mm, 151 mm and 40 mm respectively. A rubber gasket was used to seal the two PVC blocks on either side of the membrane in order to prevent leaks.

3.4 Assembly of rig and materials of construction

Please see Appendix B for step by step instruction on the assembly of the rig as well as the materials of construction used.

3.5 Chemicals required

The following chemicals were used in order to perform laboratory scale test work;

- Aluminium Sulphate powder supplied by Kimix, 97% Assay of the formula:$Al_2(SO_4)_3 18H_2O$
- Concentrated hydrochloric acid supplied by Kimix, 32wt%
- Deionized water obtained from the in-house Reverse Osmosis unit at the Department of Process Engineering, Stellenbosch University.
- Concentrated sulphuric acid supplied by Kimix, 98wt%.
- Atomic Absorption Spectrophotometer aluminium standard of 1000 ppm supplied by Kimix

3.6 Water treatment residuals feed preparation

Water treatment residuals were obtained in sludge form from evaporation ponds and HCl acid digestion was consequently done prior to Al^{3+} recovery. Two feed digestions with 0.5 M and 0.05 M HCl acid solutions were prepared.

For the first digestion, 30 grams of sludge was digested in a 1 Litre, 0.5 M HCl acid solution. A total of 3 litres was made for the feed solution.

30 grams of sludge was also used for the second digestion, however the sludge was digested in 1L of 0.05M HCl acid solution. Again a 3L feed solution was made up.

Both feed solutions were digested for a 24 hour period, then subsequently filtered.

3.7 Nafion 117

3.7.1 Activation of the membrane

The Nafion 117 membrane was activated by conditioning the membrane in a 3 % HCl warm solution at an elevated temperature of about 90° C. This is done for an hour, where after the membrane is then removed and rinsed off with deionized water for about 15 min (Napoli et al., 2013).

The membrane was further immersed in a dilute (1 % HCl) solution for 3 hours further. The last step after this is to rinse off the membrane with deionized water for about 15 min. The membrane is now activated, hydrated and ready to use (Napoli et al., 2013).

3.7.2 Cleaning and storing of the membrane

Once experimentation is done, the membrane is simply rinsed off with deionized water to remove any abrasive chemicals or compounds on its surface. It is then set out to dry and then stored away in an airtight container.

3.7.3 Membrane recovery

For reuse the membrane is immersed in a 1% aqueous HCl acid solution for 3 hours. After this, it is rinsed off with deionized water for about 15 min.

3.8 Experimental procedure

3.8.1Start up

A 3 litre feed solution with the specified aluminium sulphate run concentration was prepared. Similarly, a 1 litre sweep solution with the specified hydrochloric acid run concentration is prepared.

3.8.2 Operation

The feed and sweep peristaltic pumps were set to the required flowrate and the start time of experiment noted. Samples of the feed and sweep were taken in two hour intervals using a pipette and sampling tubes. The experimental duration was 48 hours.

3.8.3 Shutdown

After 48 hours of operation, both pumps were switched off, the contents of the feed and sweep side containers were emptied into liquid waste containers.

De-ionized water was then added to the empty containers, both pumps were switched on so that the water could circulate and clean the system. After 15 minutes both pumps were switched off and the deionized water in the containers emptied.

The Nafion membrane was taken out of the PVC blocks and immersed in 1% hydrochloric acid in order to saturate the membrane with hydrogen ions.

3.9 Analytical techniques

3.9.1 Atomic Absorption Spectroscopy (AAS)

Two analytical techniques were used for this project. The first technique was Atomic Absorption Spectroscopy (AAS). The machine used was designed by Analytik Jena model number 400P NovAA and was used in order to analyze and quantify the relative aluminium concentrations in the feed and sweep side samples. The operating procedure of the machine is provided in Appendix F-1.

3.9.2 Ultra violet visible Spectrophotometer

The second technique and machine used was an Ultra Violet-visible (UV-Vis) spectrophotometer machine designed by Varian (model 3E). It was used in order to determine the relative amounts of organics in the feed and sweep solutions of the water treatment residuals used. The operating procedure is provided in Appendix F-2.

3.10 Full factorial design

A full factorial was chosen as the design of choice because it takes into account all the possible combinations that can result from the interactions of the variables under consideration. The full factorial design also served as an experimental design which does not investigate centre point experiments (and hence less time consuming) because the objective of this part of the project was to only investigate the effect of the chosen variables at their extreme operating conditions in order to determine their effect on the final aluminium recovery and concentration more explicitly. Four variables, namely, feed concentration (F Conc), sweep concentration (S Conc), feed flow rate (F Flow) and sweep flow rate (S Flow) were chosen as starting point for this investigation based on the literature and findings of Prakash (2004).

According to Montgomery and Kowalski (2013) if an experiment has four variables and a full factorial design is used, then, the number of experiments to be performed is determined byX^n, where X is the number of levels and n are the number of variables. If two levels are used, -1, 1(low, high) with four variables, then the total number of experiments that need to be conducted will be 16 (Montgomery and Kowalski, 2013). Tables 3-1 and 3-2 below provide the variable combinations to be tested (coded values) as well as their actual values. The variable values were chosen as a starting point for the investigation as they were similar to those used by Prakash (2004) in his study.

Table 3-1: Coded values of full factorial design to be investigated

Run	F Conc	S Conc	F Flow	S Flow
1	-1	-1	-1	-1
2	1	-1	-1	-1
3	-1	1	-1	-1
4	1	1	-1	-1
5	-1	-1	1	-1
6	1	-1	1	-1
7	-1	1	1	-1
8	1	1	1	-1
9	-1	-1	-1	1
10	1	-1	-1	1
11	-1	1	-1	1
12	1	1	-1	1
13	-1	-1	1	1
14	1	-1	1	1
15	-1	1	1	1
16	1	1	1	1

Table 3-2: Actual values of the full factorial design

Code	F Conc	S Conc	F Flow	S Flow
-1	2000 mg/L	1.0 M	2.2mL/s	2.2mL/s
1	3000 mg/L	2.0 M	4.9 mL/s	4.9 mL/s

3.11 Box Behnken

While a full factorial design takes into account all the extreme possible combinations of the system, it is also a very expensive and time consuming design to investigate.

A Box Behnken design was chosen for the optimization section. The Box Behnken design utilized three factors at three different levels to evaluate the relationship between variables and their effects. In addition, the three levels make it possible for model development through least squares regression. The curvature the three levels provide in model development makes it possible to represent the responses of the variables using Response Surface Methodology (RSM). Lastly, the Box Behnken design also consists of three runs conducted at the same conditions in order to test the repeatability of the process (Montgomery and Kowalski, 2013).

Tables 3-3 and 3-4 provide the variable combinations to be tested (coded values) as well as their actual values.

Table3-3: Coded values of Box Behnken design to be investigated:

Run	F Flow	F Conc	S Conc
1	-1	-1	0
2	1	-1	0
3	0	0	0
4	-1	1	0
5	1	1	0
6	-1	0	-1
7	1	0	-1
8	0	0	0
9	-1	0	1
10	1	0	1
11	0	-1	-1
12	0	1	-1
13	0	-1	1
14	0	1	1
15	0	0	0

Table 3-4: Actual values of the Box Behnken design

Code	F Conc	S Conc	F Flow
-1	300 mg/L	0.25 M	3.5 mL/s
0	500 mg/L	0.5M	4.5 mL/s
1	700 mg/L	0.75M	5.5 mL/s

3.12 Equipment commissioning

Before experimentation commenced, the pumps were calibrated and the laboratory rig commissioned. A stop watch and beaker method was used for this with the aid of a Randomized Complete Block Design for the pump calibration.

The objective of the randomized complete block design is to "create homogeneous sets of experiments (blocks) in which the nuisance factor is held constant and the factors of interest are allowed to vary. The runs are divided into blocks such that the variability within blocks is less than variability between blocks" (Montgomery and Kowalski, 2013).

The advantage of the randomized complete block design is in its ability to reduce the residual error in an experiment by removing variability due to a known and controllable nuisance factor (Montgomery and Kowalski, 2013).In this case the nuisance factor is the pump motor temperature variability with time which in turn affects pumping power output. The blocking part is used to eliminate the effect of the most significant nuisance variable (Temperature with time), randomization is used to further reduce the contaminating effects of other not so important nuisance variables (Montgomery and Kowalski, 2013). Four sets of runs (blocks) were conducted, where four different randomized experiments calculating the flow rate at each pump setting in each block were done. Table 3-5 below shows the randomized complete block design used. Each block (1-4) consists of four different pump setting runs (in terms of percentage flow rate of the pump). In order to calculate the average pump flow rate at a specific setting, the flow rates obtained in each Block were added together and then averaged.

Table 3-5: Randomized Block Design

	Test coupon (Block)		
1	2	3	4
75%	75%	50%	25%
25%	100%	25%	100%
100%	50%	75%	50%
50%	25%	100%	75%

Following this, the equipment was commissioned and then leak tested. The leak testing procedure may be seen in Appendix F-3

Chapter 4 Results

4.1 Introduction

This chapter is divided into four sections. The first section provides a validation of all experimental runs performed based on mass balance closures and repeatability. The following section is the investigative section which discusses all the investigative runs performed, their operating conditions and maximum recoveries achieved. Following this section is the modelling and optimization section which builds on the investigative section to further improve recoveries. Lastly, runs and test were performed on real WTRs and the results and findings are discussed here.

4.2 Validation of experimental runs performed

This section focuses on the validation of experimental runs performed by using both mass balance closures and repeatability analysis. The repeatability analysis was done to ensure the reliability of the results obtained from experimental work. The mass balance part was done to ensure that no mass was lost from the experimental rig by either deposition in the rig or from leaks.

4.2.1 Error analysis

The repeatability analysis was performed by repeating a run under the exact same operating conditions two times then subsequently analysing the data with the AAS machine. The run was performed with a feed concentration of 500 mg/L of aluminium, 0.5 M HCl and a flow rate of 4.5 mL/s. The analysis calculated was inclusive of both the experimental error as well as the analysis error. However, graphs in Appendix D have been included for the error analysis of the AAS machine. There, runs using the same concentrations of aluminium were repeated over a few days to test the accuracy and repeatability of the AAS analysis technique.

In sections 4.2 and 4.4 straight lines have been used to connect the data points solely for the purpose of guiding the eye. These are not intended to reflect the relationships between the variables considered, this is dealt with in section 4.2.2.

Figure 4-1 illustrates the feed and sweep profiles of the repeatability run performed.

.

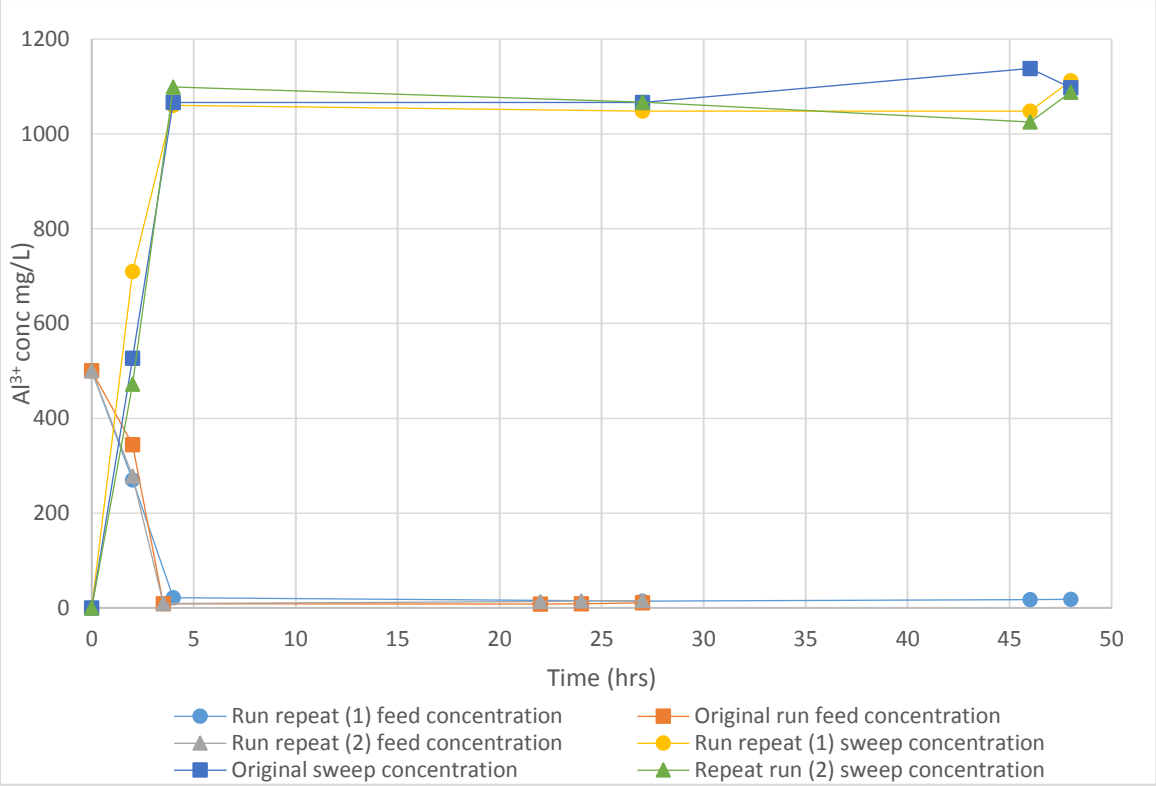


Figure 4-1: Repeatability runs for error analysis

Due to experimental initial conditions varying vastly from run to run, conventional methods of measuring error such as standard deviation, maximum and minimum error as well as standard error could not be used. Instead percent deviation was used. The percentage deviation measured the degree to which individual data points in a statistic deviated from the average measurement of that statistic (similar to standard deviation). Therefore, the mean was determined and then the average deviation of data points from that mean was used. The use of the percentage deviation allowed for errors of experimental runs with different initial operating conditions to also be calculated. Sample calculation are provided in Appendix B.

Errors were calculated for both the feed and sweep results. Data at different time intervals from both the original run and its two subsequent repeat runs was collected and grouped, then an error for each time interval was calculated. Data from the feed and its two subsequent repeat runs was collected at time 2 hrs, 4 hrs, 22 hrs, 24 hrs, 27hrs, 46 hrs and 48 hrs. Based on this, an error for each time interval was then calculated. Figure 4-2 illustrates the feed side run and its associated errors for each time interval. Figure 4-3 depicts the same but for the sweep side.

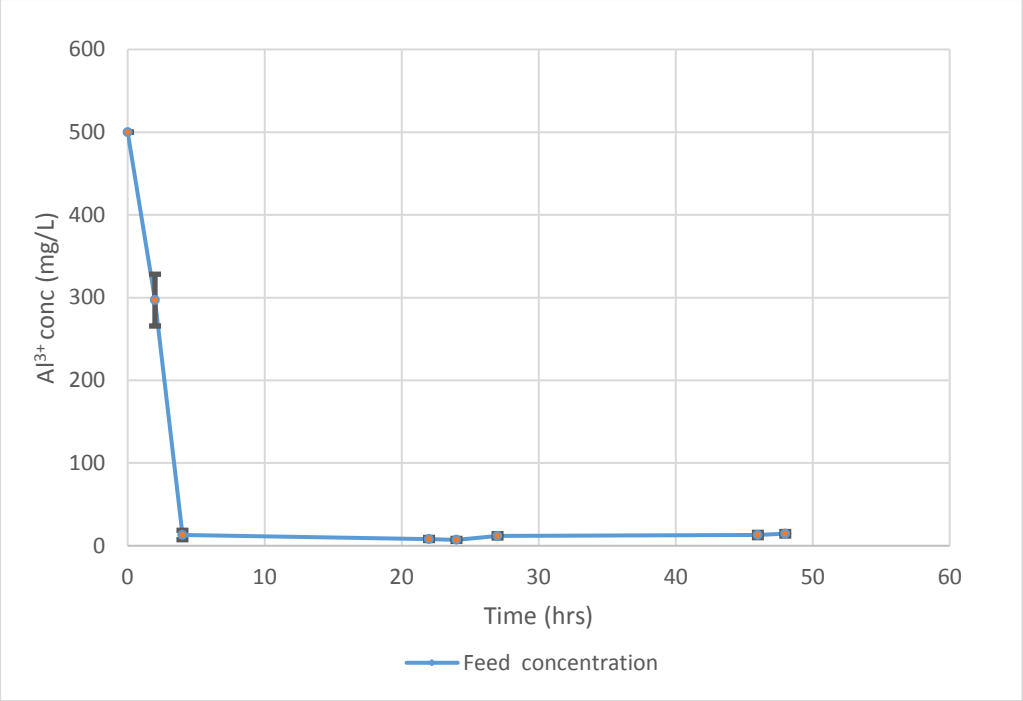


Figure 4-2: Aluminium ion feed profile and % error

The largest aluminium ion concentration errors bars were found to be between zero to four hours as this was the region most sensitive to the timing of sampling due to the concentration gradient being extremely steep. Secondly, this corresponded to the start-up stage of the run, which was where the greatest disturbances occurred largely due to pumps starting up, non-uniform mixing and the membrane surface not being fully in contact with the feed and sweep side solutions. After this stage, the experimental error for the duration of the run was found to be smaller. Table 4-1 displays the percentage deviation from the mean associated with each time interval that was used to calculate the errors for Figure 4-2.

Table 4-1: Average and % deviation of feed for error analysis

Time (hrs)	Mean (mg/L)	Average deviation (mg/L)	% deviation
0	500	0	0.0
2	297	±31.3	10.5
4	13	±5.7	42.9
22	8.2	±1.9	22.9
24	7.1	±1.8	24.8
27	12	±2.6	21.7
46	13	±3.2	23.2
48	14.5	±2.7	18.5

The error analysis for the sweep side is displayed in Figure 4-3 below. Table 4-2 also provides the average and percentage deviations for the sweep side analysis.

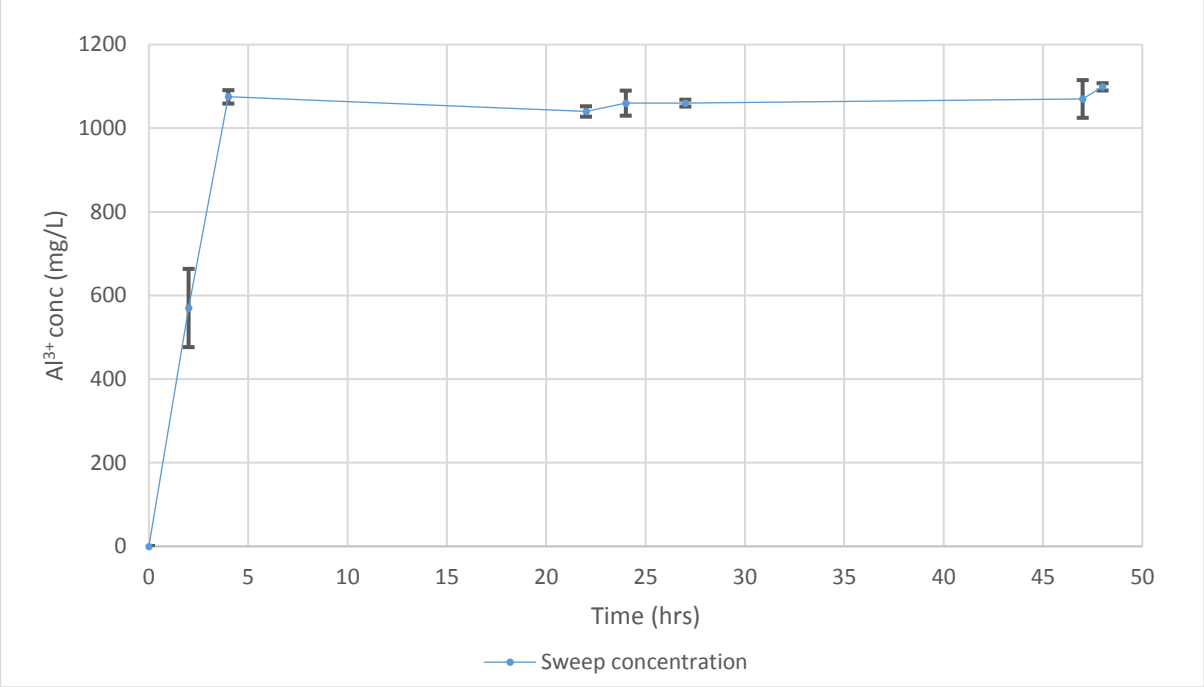


Figure 4-3 Aluminium ion sweep profile and % error

Table 4-2: Average and % deviation of sweep for error analysis

Time (hrs)	Mean (mg/L)	Average deviation (mg/L)	% deviation
0	0	±0	0.0
2	570	±93.6	16.4
4	1075	±16.0	1.5
22	1040	±12.4	1.2
24	1060	±30.0	2.9
27	1060	±8.2	0.8
46	1070	±45.1	4.2
48	1099	±8.7	0.8

4.2.2 Mass balance and verification

A run was conducted in order to determine mass balance closures and to determine if the Donnan Dialysis process results could be accurately used for quantification. The run was conducted using a concentration of 3000 mg/L of aluminium and 2M sulphuric acid sweep concentration. The initial feed volume was 3 L and that of the sweep was 1 L. The flow rate was kept constant at 4.9 mL/s and 10 mL samples were taken at regular intervals in order to determine the concentration profile of the run. Table 4-3 displays the initial and final aluminium ion concentration in both the feed and sweep with the use of the AAS machine. The operating conditions were chosen as they were identical to those conducted by Prakash (2004), hence by comparing the results it would be immediately possible to discern if the run performed was similar to those stated in literature. For this section a trend line was used in order to guide the eye and to illustrate the relationship between the variables concerned.

Table 4-3: Mass balance of verification run

	Initial mass of Al^{3+} (mg)	Final mass of Al^{3+} (mg)
Feed	9300	1203
Sweep	0	7980
Total	9300	9183
% difference	1.26	

It can be seen that the mass difference in and out was about 1.3%. This is excellent and shows that all the aluminium ions remained in solution and was accounted for within the accuracy of analysis. The corresponding corrected (change in volume of the feed and sweep taken into account) feed and sweep side concentrations of the run for the mass balance above is illustrated in Figure 4-4.

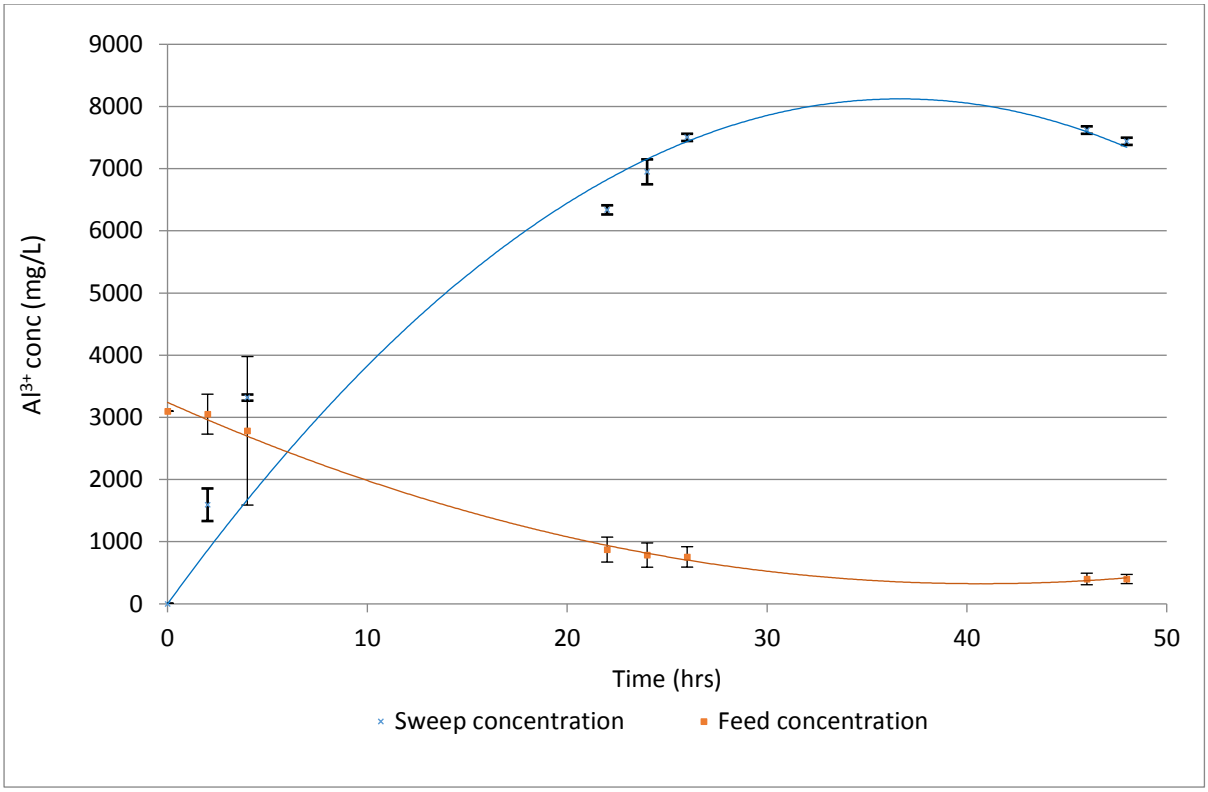


Figure 4-4: Corresponding mass balance and verification run feed and sweep profiles

The first major observation from Figure 4-4 is that it is possible to concentrate a feed solution containing Alum by about 2.5 times. The starting feed concentration was 3000 mg/l of aluminium (orange line at time= 0 hrs) and was concentrated to 7500 mg/L in a 26-hour period. Trend lines were then fitted on to the data to depict the relationship between the concentration of the feed and sweep with time. The trend lines were found to support the findings of Prakash (2004).

It is not intuitively obvious that this is possible, since the equilibrium in 'normal' mass transfer processes occurs when the feed and sweep concentrations are the same. An illustration of such a typical mass transfer operation without an external force being applied such as pressure is displayed in Figure 4-5. The feed side (blue line) starts at a much higher concentration and the sweep side (orange line) starts with no concentration. The feed steadily decreases in concentration while the sweep steadily increases with time, until the point at which both feed and sweep concentrations are the same, then no more mass transfer occurs due to a lack of driving force.

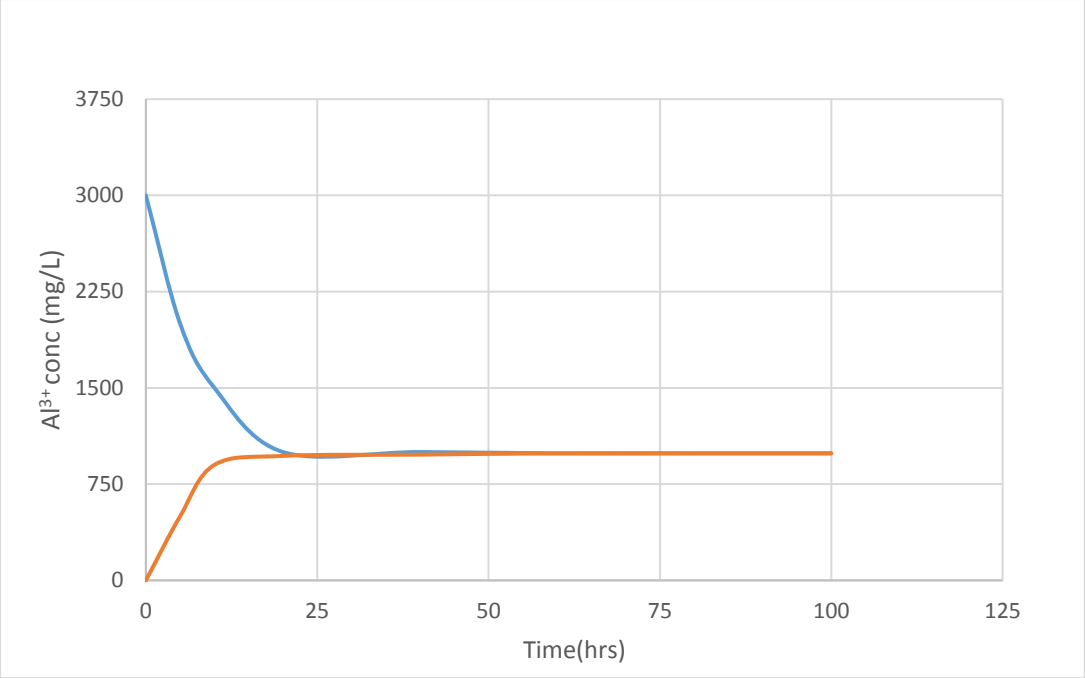


Figure 4-5: Example of "Normal" mass transfer process with no external driving force

For Donnan Dialysis, as is evident in Figure 4-4, this is not the case. This phenomenon is due to the fact that the equilibrium in a Donnan Dialysis process is both charge and concentration related. Aluminium has a charge of 3+ and Hydrogen 1+. This great difference in the charges/valences between the particles provides the driving force necessary to concentrate the aluminium ions (Davis, 2001). A high initial concentration of the substitute ion, in this case hydrogen results in a high final concentration of the target metal ion (aluminium). Secondly, the higher the ionic charge of the target metal to be recovered and the lower the ionic charge of its substitute ion are, the higher the recovery and final concentration of the target metal will be (Davis, 2001). Equation 3 in the section 2.2 provides an understanding of the exact mechanism of this.

The lowest concentration in the feed side was found to be 400 mg/L after about 48 hours. It is worth noting though that Figure 4-4 provides an indication that after about 24 hours of operation, not much aluminium concentrating takes place in the sweep and the kinetics become extremely slow. In fact, the concentration of aluminum decreases towards the end. This was hypothesized by Prakash (2004) to be due to the dilution of the concentration of the sweep due to an osmotic phenomenon. The results yielded from this initial investigation showed promise and provided proof that recovering and concentrating aluminium with the use of Donnan Dialysis is possible.

At the end of the mass balance and verification run, it was found that roughly 400 mL of water had decreased in the feed side reservoir (feed now 2600 mL), and 400 mL of water had increased in the sweep side reservoir .This volume change was taken into account when performing the mass balance and verification run above. As a consequence of this, before further runs could be done, an investigation to understand this hydrodynamic effect was undertaken. It is discussed in the next section.

4.3: Hydrodynamic transport

4.3.1: Introduction

The phenomenon of water flux observed in the previous verification section is a critical issue, its consequences and severity have been greatly underplayed in literature. It poses to negate part of the work of concentrating Water Treatment Residuals using Donnan Dialysis as the water transported across the membrane dilutes the concentrated aluminium ions. An understanding of why and how it happens is thus essential in order to mitigate this transport as much as possible.

Consequently, multiple investigations were conducted in order to better understand the water transport effects through a Nafion 117 membrane. They are discussed in section 4.3.2.

4.3.2: Results

The objective of the first experiment was to determine if water was being transported across the membrane as a result of a pressure variation across the membrane.

For the first experiment, 3 L of water was added to the feed side and 1 L to the sweep side. The experiment was run for 50 hours to determine if there would be any water transport through the membrane from the feed or sweep side. At the end of the run no volume change in the feed and the sweep was observed, hence water transported due to pressure variations across the membrane was rejected as the explanation for the behavior in Section 4.2.2.

As water transport due to equipment and the setup was dismissed, the aim of the next series of experiments was to investigate if the water transport in the system was due or related to the chemicals used in the runs. All the chemicals used were subsequently investigated, however in order to ensure that some effects did not cancel each other out, the chemicals were added at different stages. I.e. a chemical was added, then a run was conducted to see the effect of that chemical, then another chemical was added and a run was subsequently added.

Given that, a second run was then conducted where 3000 mg/L of aluminium was added to 3 L of water in the feed. The sweep side was run with 1 L of water. The experiment was conducted for a period of 50 hours. At the end of the run, no volume change was observed.

Acid was then added to the sweep side to make a 1 L solution of 2 M HCl. The feed side was kept at 3 L and an aluminium concentration of 3000 mg/L. The duration of the experiment was 48 hours. At the end of the run it was found that the volume of the feed decreased by roughly 700 ml and that of the sweep increased by the same amount. These results showed that the transportation of water across the membrane occurred only when there was ionic exchange from species in the feed (Al^{3+}) and species in the sweep (H^{+}) through the membrane. This observation supported the work performed by Okada et al. (1998). They suggested that water transport through the membrane occurred due ions ‘pushing’ water molecules through membrane channels by volume exclusion.

The fourth run which was conducted investigated the interaction between acid and water transport through a Nafion membrane. 3 L of water was added to the feed side and a 1 L sweep solution containing 2 M HCl was used for the run. The experiment was conducted for a period of 48 hours. A volume change was observed at the end of the run. The feed side decreased by 400 mL and the sweep side increased by 400 mL. Since water could not be transported through the exchange of ions through the membrane as there was no aluminium present, a secondary factor played a role in the transport of water.

Further runs were then conducted to determine the effect of changing the concentration of HCl on the volume of water transported. Figure 4-6 illustrates these runs.

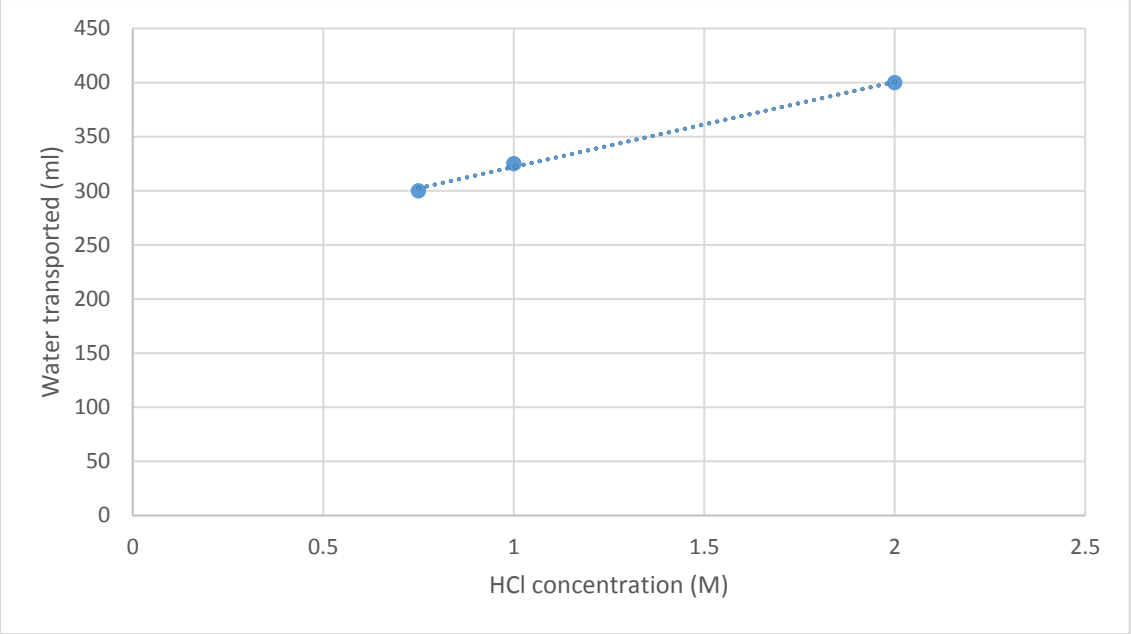


Figure 4-6: Effect of water transport volume with varying HCl concentration

It can be seen that the volume of water transported from the feed to the sweep side was found to be linearly proportional to the concentration of hydrochloric acid used. A straight line was fitted on to the data points to verify this, the coefficient of determination was found to be 0.99 (indicating that 99% of the variation in the data was explained by a linear trend). The temperature and pressure were not varied throughout the runs done. This therefore meant the only parameter which was altered was concentration. With that in mind, the secondary factor affecting the transportation of water was hypothesized to be osmotic pressure. Osmotic pressure for ideal solutions is defined as:

$$\pi = iMRT \qquad \text{Equation 4-1}$$

Where π is the osmotic pressure

i is the Van't Hoff factor

M is the molar concentration of species

R is the ideal gas constant

T is the temperature

If this hypothesis were to be true, then the following would need to be true or answered as well:

1. Acids at the same temperature having the same concentration as HCl but having higher osmotic pressure (i.e. higher Van't Hoff factor) would be able to draw more water through the membrane.
2. If osmotic pressure was the reason, then why did aluminium ions in the feed not draw water from the sweep side to the feed?

In order to answer and verify the question and statement above, a graph of osmotic pressure verses concentration was calculated and drawn using equation 4-1(a temperature of 298 K was used) . It may be seen in Figure 4-7.

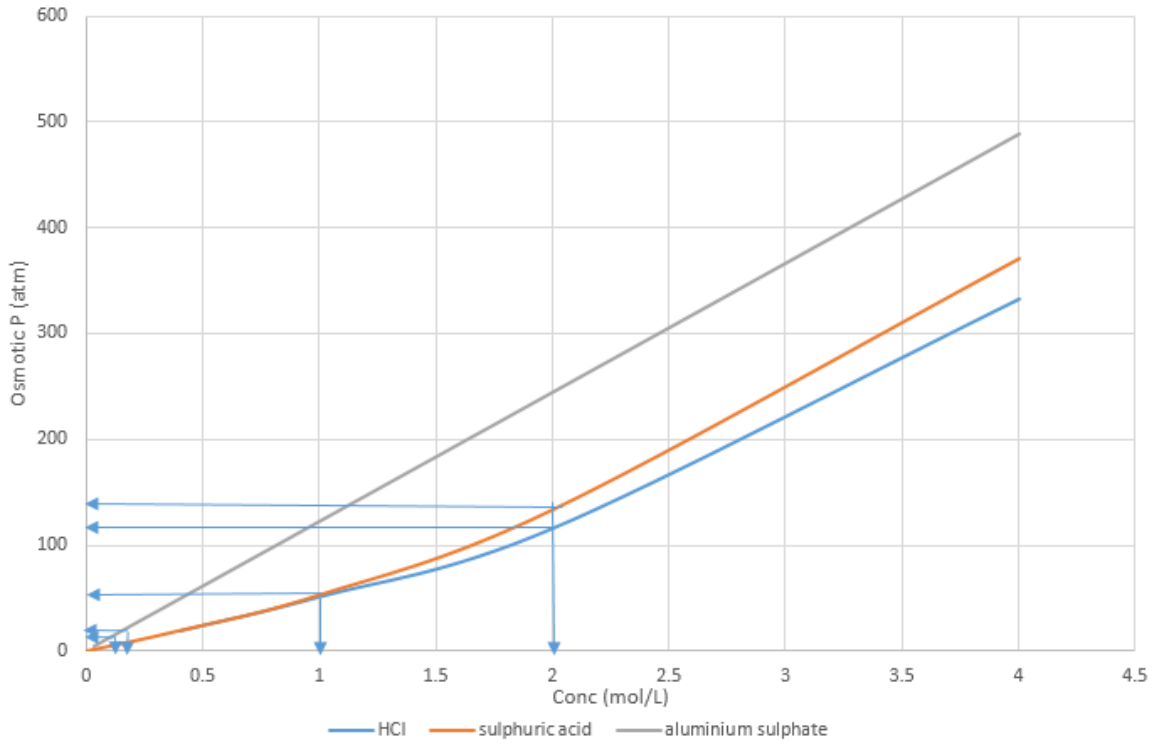


Figure 4-7: Effect of sulphuric acid, hydrochloric acid and aluminium sulphate concentrations on osmotic pressure

Figure 4-7 serves to provide theoretical proof that acids at the same temperature having the same concentration as HCl but having a higher Van't Hoff factor would be able to draw more water through the membrane because they would have a higher osmotic pressure. As osmotic pressure increases in a system, the capacity of that chemical species causing the increase to withdraw or "pull" water across a membrane also increases. This means an increase in osmotic pressure results in a proportional increase in water which is withdrawn or "pulled" across the membrane.

Figure 4-7 depicts three lines, which illustrate the relationship of concentration with osmotic pressure of the three chemical species used in the Donnan Dialysis experimentation. For all three of these chemical species, it is evident that as their concentrations increase, so too does the osmotic pressure of the system. If the concentrations of the three species were to be kept constant at 2 M, then the graphs show that aluminium sulphate has the highest osmotic pressure, followed by sulphuric acid and then hydrochloric acid. If the same concentration of all species were used, then the aluminum sulphate would be able to "pull" or transport the most water across the membrane, followed by sulphuric acid then hydrochloric acid. The concentration range of aluminium sulphate however used for the investigations of this project were very low. The range is shown by where the black lines meet the grey line on the x –axis, and the corresponding pressure range is also shown on the y-axis. The same has also been done for the sulphuric acid and hydrochloric acid concentration range and osmotic pressure range. The low concentration range of aluminium sulphate used in the experimentation is the reason why aluminium ions were not able to draw water from the sweep side to the feed.

From Figure 4-7 it evident that for concentrations greater than 1M, sulphuric acid (higher Van't Hoff factor than HCl) has a greater osmotic pressure than hydrochloric acid

In order to verify this experimentally as well, another experiment was conducted and it was found that the water transported across the membrane due to osmotic effects by sulphuric

acid at the same concentration as HCl was higher. It was found that 750 mL was transported from the feed side to the sweep side using sulphuric acid, as opposed to the 400 mL that was obtained when using hydrochloric acid.

Lastly, the question of why aluminium in the feed did not cause water transport across the membrane may be answered by Figure 4-7 above. The arrows from the aluminium sulphate line pointing toward the X and Y axis indicate the upper and lower concentration boundaries the investigations were conducted at, as well as their corresponding osmotic pressures. The osmotic pressure values due to aluminium are seen to be very low (10-30 atm). The resulting water that would have been transported through the membrane due to aluminium osmotic effects would have therefore been almost negligible.

Given the above arguments, it can be concluded that water transport through the membrane can be attributed to osmosis as well. Investigations conducted by Prakash and Sengupta (2003) as well as Prakash (2004) further support this result and conclusion.

4.3.3: Summary

An investigation was done in order to determine and quantify the hydrodynamic effects taking place in the verification run. Water was found to be transported from the feed side to the sweep side through osmotic transport. It was found that at the same temperature and pressure, the volume of water transported across the membrane (from feed to sweep) was linearly proportional to the concentration of acid used. Secondly, the concentration of the sweep was found to be linearly proportional to osmotic pressure. Through these relationships it was then expected that the volume of water transported would be linearly proportional to osmotic pressure. Moreover, it was determined that different acids at the same concentration having different Van't Hoff factors such as sulphuric acid (higher Van't Hoff factor) and hydrochloric acid (lower Van't Hoff factor) transported water differently. The acids with a higher Van't Hoff factor were found to transport a higher volume of water across than acids with a lower factor. Experimentally, 2M hydrochloric acid was found to transport 400 mL of water while 2M sulphuric acid was found to transport 750 mL.

Given the results that the same molarity of sulphuric acid was able to draw more water than hydrochloric acid across the membrane leading to more dilution, hydrochloric acid was used in subsequent experimentation in order to mitigation the dilution of the concentration in the sweep via osmotic transport.

4.4: Screening runs

4.4.1: Introduction

The objective of this section is to investigate the effects of feed concentration, sweep concentration, feed flow rate and sweep flow rate on the amount of aluminium which can be concentrated through the Donnan Dialysis process. The variables and their respective operating conditions were chosen as a good starting point for this investigation after numerous consultations from Prakash (2004), Van Rooyen (2012) and Prakash and Sengupta (2003). An experimental run time of 46- 48 hours was also decided upon for the same reason. A full factorial design with 4 factors and 2 levels was used to carry out this investigation. In addition to previous studies from literature pointing out the selected variables and their operating conditions were a suitable start for this investigative, the selection of the extreme operating conditions chosen would also provide a more noticeable effect on the recovery of aluminium. For this section a trend line was used in order to illustrate the relationship between the variables concerned.

In order to assess both the effect of these variables on hydrodynamic transport as well as the amount of aluminium recovered, concentration was chosen as the response factor. Lastly, in order to represent the trends of the four variables, eight of the possible graphs will be used for comparison in each section. The remaining data for the runs can be seen in Appendix A. Table

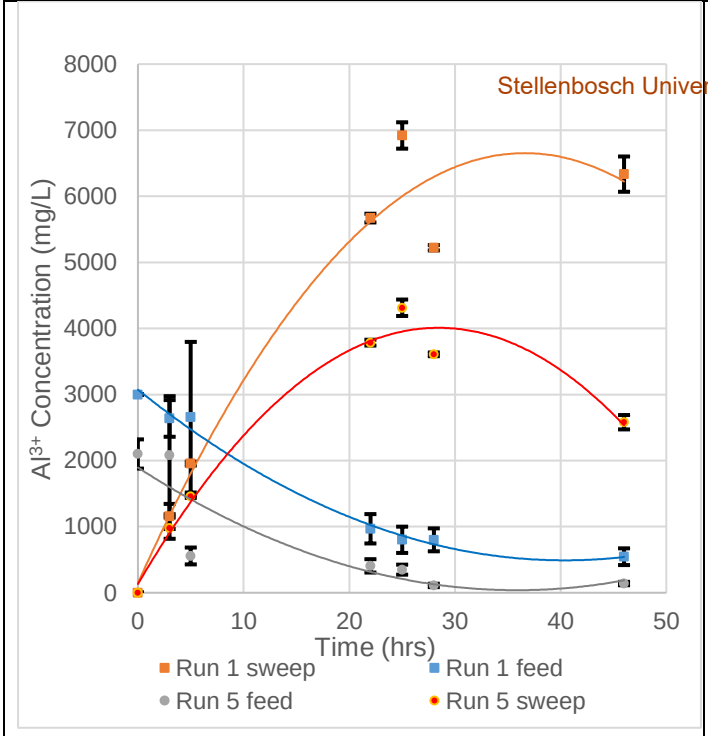
4-4 may be used as a key for the runs which will be used throughout this section and their corresponding conditions.

Table4-4: Key for runs to be used

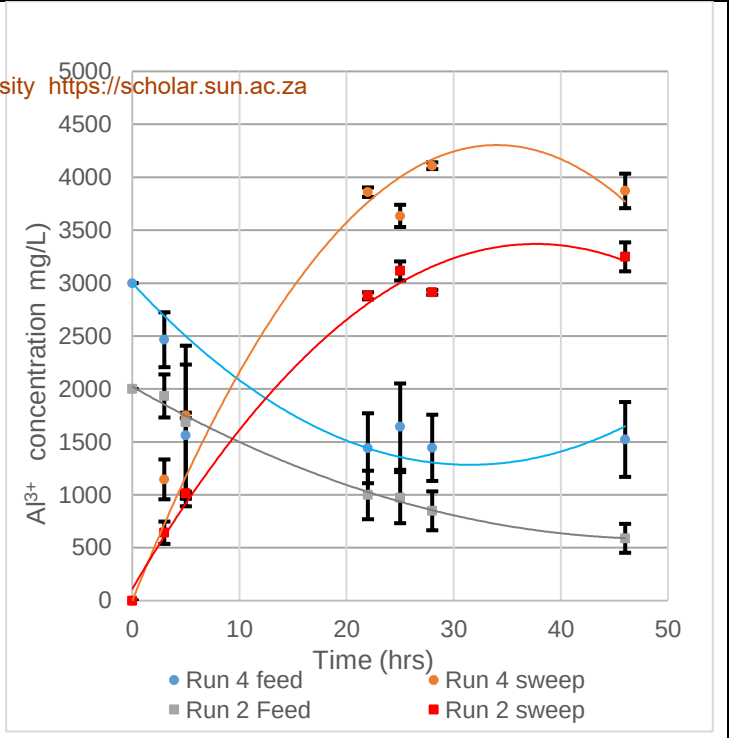
Run	Conditions			
	Aluminium feed conc (mg/L)	HCl sweep conc (M)	Feed flow (mL/s)	Sweep flow (mL/s)
1	3000	2	2.2	2.2
2	2000	1	4.9	4.9
3	3000	1	2.2	2.2
4	3000	1	4.9	4.9
5	2000	2	2.2	2.2
6	3000	2	4.9	4.9
7	2000	1	2.2	2.2
8	2000	1	4.9	2.2
9	2000	1	2.2	4.9
10	3000	1	4.9	2.2
11	2000	2	4.9	2.2
12	3000	2	4.9	2.2

4.4.2: Effect of Feed concentration

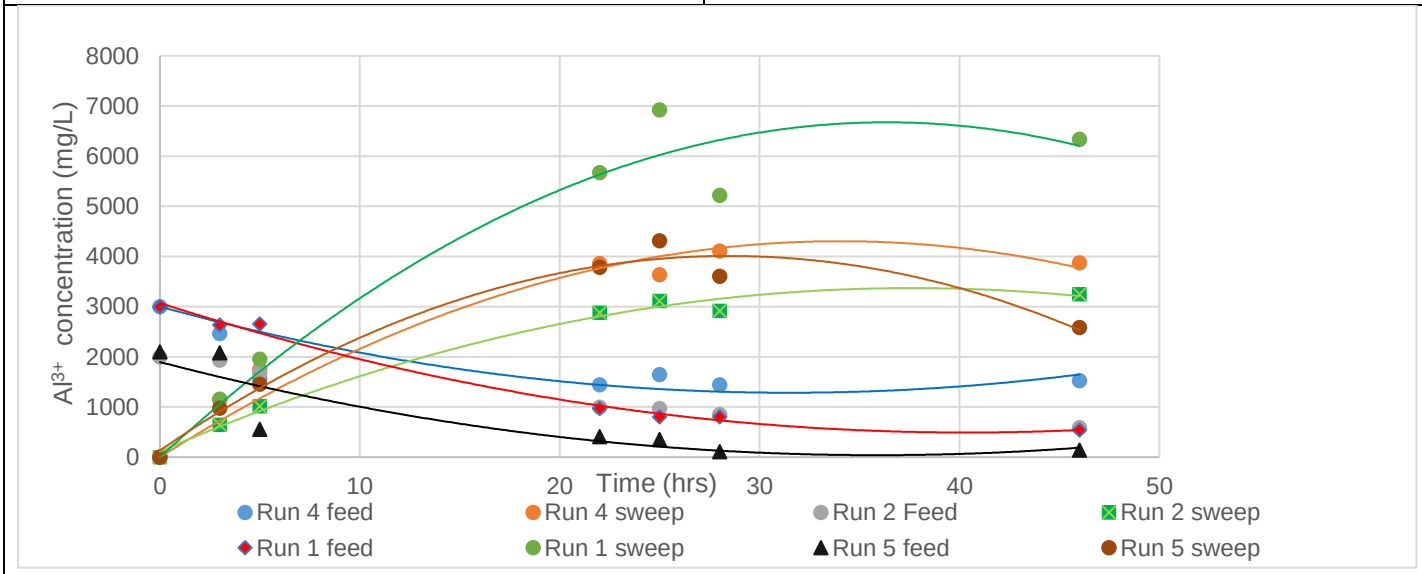
In order to assess the effect of feed concentration, Runs 1 and 5 will be compared as well as Runs 2 and 4. For Runs 1 and 5, the sweep concentration, feed flow and sweep flow were held constant at 2 M, 2.2 mL/s and 2.2 mL/s while the feed concentration was varied from 2000 mg/L to 3000 mg/L. For Run 2 and 4, the sweep concentration was fixed at 1M, feed pump setting of 4.9 ml/s and sweep pump setting of 4.9 ml/s. The feed concentration was also



(A) High initial acid concentration, low flow rates, varying initial feed concentration



(B) Low initial acid concentration, high flow rates, varying initial feed concentration



(C) Comparison of all runs conducted for the effect of initial feed concentration on final aluminium ion concentration

Run	Conditions(feed conc, sweep conc, feed flow rate, sweep flow rate)
1	3000 mg/l 2M 2.2 mL/s,2.2 mL/s
5	2000 mg/L 2M 2.2 mL/s,2.2 mL/s
4	3000 mg/L 1M 4.9 mL/s, 4.9 mL/s
2	2000 mg/L 1M 4.9 mL/s, 4.9 mL/s

Figure 4-8: Effect of feed concentration at constant sweep concentration, feed flow rate and sweep flow rate. Trend lines added for visual clarity.

From Figure 4-8A it can be seen that Run 1 operates with an initial feed of 3000 mg/L and has a final sweep concentration of 6335 mg/L. Run 5 operates with an initial feed concentration of 2000 mg/L and the final sweep concentration is 2581 mg/L. Starting with a higher concentration if the initial volumes of Run 5 and Run 1 are the same equates to starting off with a higher mass of aluminium in Run 1. It would seem that a higher initial feed concentration yields a higher final sweep concentration, intuitively this is true, but not completely accurate. More mass at the beginning will result in a larger amount of mass being recovered at the end. If instead, the final concentration of the sweep is divided by the initial concentration of the feed, the ratio obtained becomes more useful in terms of how much the final stream of aluminium can be enriched by. Doing this for Runs 1 and 5 yields 2.1 and 1.3 respectively.

Another trend which can be seen from the sweep results is that the graphs can be divided into three main sections. The first section takes place from 0 to about 5 hours and has the steepest gradient of all. The second section has a less steep incline and tapers off at about 25 hours. The last section has a decrease in concentration of the sweep. Prakash et al. (2004) investigated this previously and postulated that the first section is governed by a high electrochemical potential due to both the aluminium and acid being in abundance in the feed and sweep sides respectively. He defined this steepest section as the kinetically driven zone (this is why both Runs 1 and 5 had the highest increase in concentration in the first 5 hours). The next zone occurs between 5-25 hrs, as the concentration of aluminium decreases in the feed side and the electrochemical potential decreases, the rate of recovery of aluminium decreases. This can be seen by the decrease in the gradient, this section is termed the Donnan equilibrium zone and is governed by the Donnan Dialysis equation described in detail in section 2.2.1 (Runs 1 and 5 still increase in concentration but not as rapidly as in the time period of 0-5hrs). Lastly, when the aluminium recovered reaches a maximum in this zone it is seen to decrease again. This section of decreased concentration is predominantly characterized by hydrodynamic effects. Prakesh et al. (2004) hypothesized that water transport from the feed to the sweep side was due to osmosis and termed the zone as the “osmosis driven” zone. While osmosis occurs continuously in the system, after 25 hours of operation, Donnan equilibrium is approached and osmosis effects dominate and reduce the sweep concentration. These trends are discussed further in section 2.2.2. This hydrodynamic transport serves to explain the profile of the sweep concentrations of Run 1 and Run 5 at about 25 hrs into the experiment

The hydrodynamic transport behavior also servers to explain why the maximum sweep concentration at 25 hours for Runs 1 and 5 didn’t correspond to a minimum in the feed section at that time. Looking at both the feed trends of Run 1 and 5, aluminium is still being transported from the feed to the sweep at this time hence the continued decrease in concentration in the feed. However, while the sweep is still receiving aluminium and the concentration should thus increase, more water from the feed is reporting in the sweep due to water transport, and as a result further dilutes the concentration of aluminium in the sweep faster than more aluminium can be transported from the feed to the sweep side to counter this.

Figure 4-8 B compares Runs 2 and 4. Similarly to Runs 1 and 5, the graph can be divided into the three zones discussed above. Namely, the kinetically driven zone from 0-5 hours, the Donnan Dialysis zone from 5-25 hours, and the osmosis driven zone from 25 hours onward. For Runs 2 and 4, the concentrating factors (ratio of final aluminium sweep concentration to initial feed concentration) obtained were 1.6 and 1.3 respectively.

Figure 4-8 C compares all of the runs on one graph. The results of the first pair (Runs 1 and 5) indicate that a higher feed concentration enriches the final aluminium concentration collected more than a lower feed concentration. The results from the second pair of runs (Runs 2 and 4) suggest the opposite. This may appear contradictory, however it means that the effect of feed concentration is heavily intertwined with the acid concentration of the sweep. Previous investigations conducted concluded that the acid concentration in the sweep is linearly proportional to the amount of water transported from the feed to the sweep. The run pair 1

and 5 were conducted at 2M acid while run pair 2 and 4 were conducted at 1M acid. Therefore more water was pulled across and thus diluted the sweep side of Runs 1 and 5 more than Runs 2 and 4. Given this, the differences in dilution amounts in the respective sweeps played a critical role in the outcome of whether or not a high initial feed concentration resulted in a higher concentrating factor or not.

This difference in acid concentrations used and thus water transported across the membrane also serves as a possible explanation as to why the sweep of Run 2 increased from 3115 mg/L at 25 hours to 3248 mg/L by the end of the run. The usual trend of the sweep observed for all runs was for it to decrease after 25 hours as the run entered the osmosis driven zone. It is hypothesized that the water transported across to the sweep for Run 2 was much less since 1M acid was used and was thus not enough to dilute the sweep at a faster rate than aluminium was being transported from the feed to the sweep.

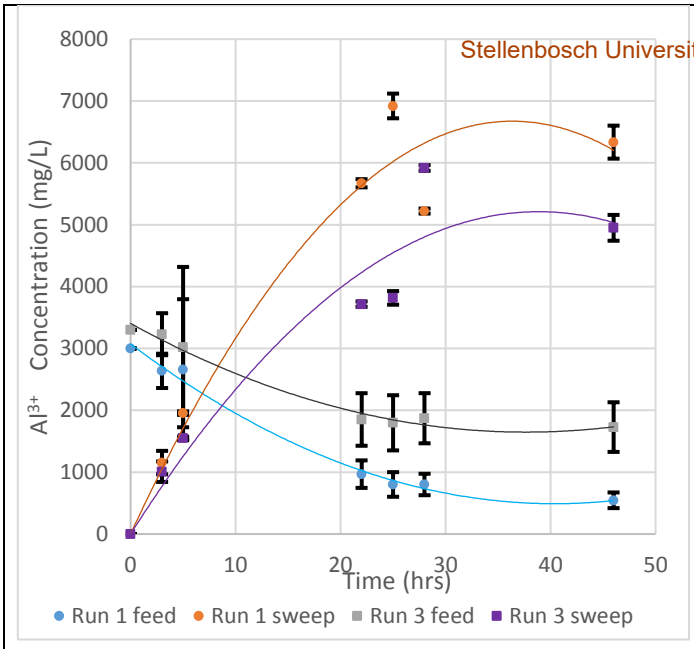
The effect of acid concentration on the amount of aluminium recovered will be discussed in the next section in order to fully understand this.

4.4.3: Effect of sweep concentration

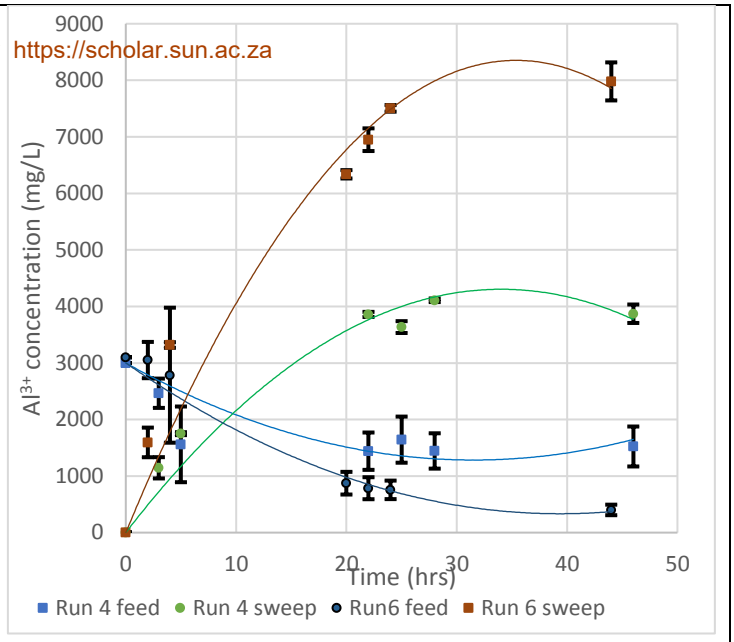
The effect acid concentration in the sweep has on the recovery and concentration of aluminium is a balance between two forces. The first is hydrodynamic transport which is linearly dependent upon the concentration of acid used. A higher acid concentration results in more water being transported across the membrane to the sweep, thus decreasing the aluminium concentration. The implication of a reduced concentration while the recovery of aluminium may be high is that it cannot be directly reused in a water treatment plant. The aluminium would therefore need a further process to concentrate it to the required levels.

On the other hand, a higher acid concentration provides faster kinetics and a higher aluminium exchange (due to more hydrogen ions being present). This is because a higher concentration firstly provides a higher electrochemical potential for the kinetically driven zone, as well as a higher ability to withdraw aluminium ion density from the feed to the sweep in the Donnan equilibrium driven zone.

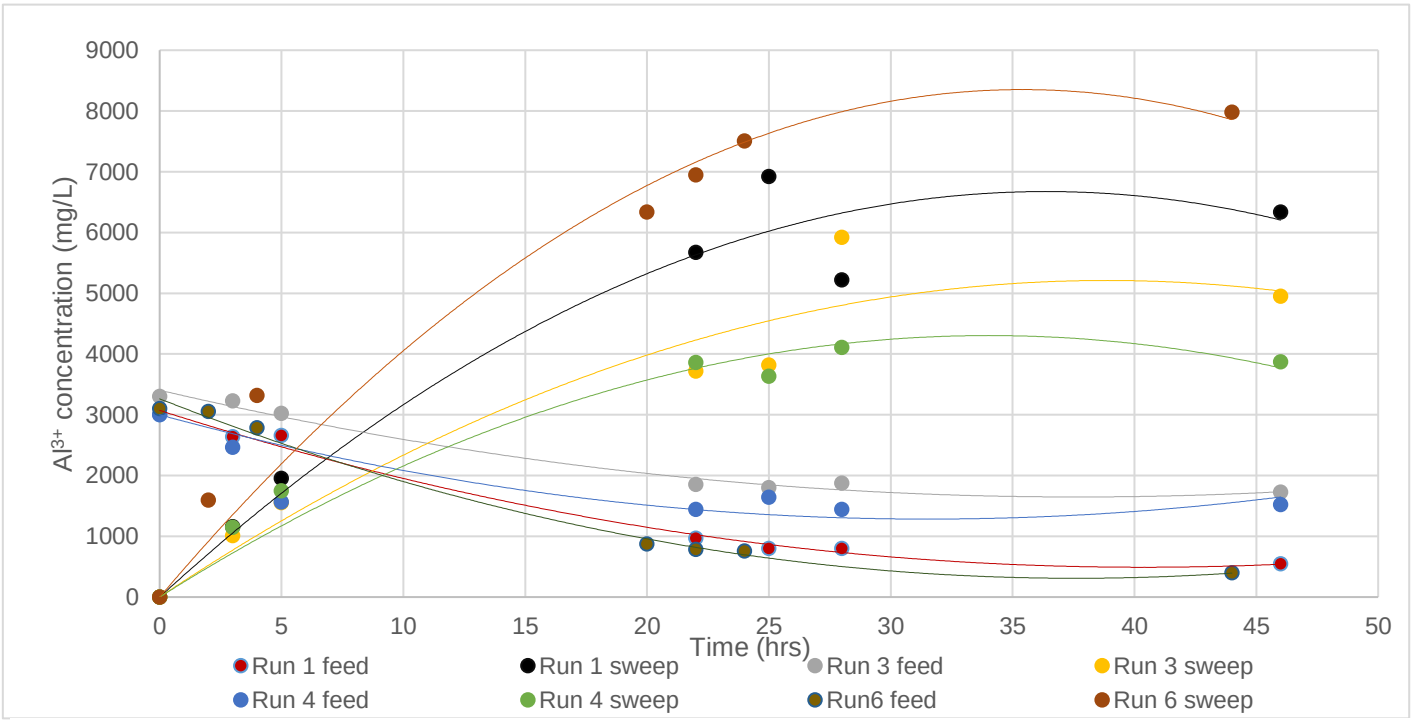
Ultimately, whichever net forces are larger will determine if a higher or lower concentration increases or decreases the final concentration of aluminium. For this investigation, Runs 1 and 3 were paired together as well as Runs 4 and 6. The Run 1 and 3 pair was operated at a 3000 mg/L feed concentration, 2.2 mL/s feed flow rate and 2.2 mL/s sweep flow rate. Run 1 was conducted at a sweep concentration of 2M and Run 3 at 1M. The run pair 4 and 6 was also operated at a 3000 mg/L feed concentration, with a 4.9 mL/s flow rate in both the feed and the sweep. Run 4 had 1M acid and Run 6 had 2M. The results of this investigation are displayed in Figure 4-9.



(A) High initial feed concentration, low flow rates, varying initial sweep concentration



(B) High initial feed concentration, high flow rates, varying initial sweep concentration



(C) Comparison of all runs conducted for the effect of initial sweep concentration on final aluminium ion concentration

Run	Conditions(feed conc, sweep conc, feed flow rate, sweep flow rate)
1	3000 mg/l 2M 2.2 mL/s, 2.2 mL/s
3	3000 mg/L 1M 2.2 mL/s, 2.2 mL/s
4	3000 mg/L 1M 4.9 mL/s, 4.9 mL/s
6	3000 mg/L 2M 4.9 mL/s, 4.9 mL/s

Figure 4-9: Effect of sweep concentration at constant feed concentration, feed flow rate and sweep flow rate. Trend lines added for visual clarity.

From Figure 4-9 A, the following can be seen: the sweep concentration of Run 3 increases to 1552 mg/L of aluminium in the first 5 hours of operation (this is the kinetically driven zone). As the process switches into the Donnan equilibrium zone between 5 and 28 hours a maximum concentration of 5918 mg/L is reached. From 28 hours the concentration starts to taper off as osmotic effects become significant. The final sweep concentration at the end of the investigation was found to be 4950 mg/L. In terms of the sweep of Run 1, the kinetically driven zone (0-5 hrs) yielded an aluminium ion concentration of 1955 mg/L, the Donnan equilibrium zone (5-25 hrs) was found to further concentrate aluminium ions to a maximum concentration of 6920 mg/L. The osmosis driven zone (25-46 hrs.) was found to dilute the aluminium concentration in the sweep to a final value of 6335 mg/L.

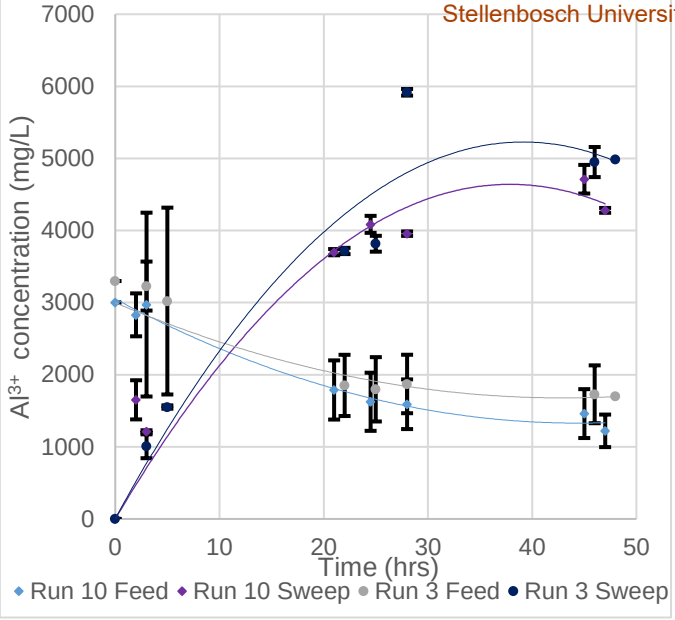
Analyzing Figure 4-9 B the trends which can be seen are as follows: the sweep concentration of Run 6 increased to 3318 mg/L of aluminium in the first 4 hours of operation (this is the kinetically driven zone). As the process switched into the Donnan equilibrium zone between 4 and 24 hours, a concentration of 7503 mg/L was reached. From 24 hours the concentration started to increase slightly. The final sweep concentration at the end of the investigation was found to be 7980 mg/L. In terms of the sweep of Run 4, the kinetically driven zone (0-5 hrs.) yielded an aluminium concentration of 1750 mg/L, the Donnan equilibrium zone (5-28 hrs.) was found to further concentrate aluminium ions to a maximum concentration of 4109 mg/L. The osmosis driven zone (28-46 hrs.) was found to dilute the aluminium concentration in the sweep to a final value of 3871 mg/L.

Figure 4-9C compares all the runs on one graph for ease of reference. The final sweep concentration of Run 1 was found to be 6335 mg/L while that of Run 3 was 4950 mg/L. For the second pair of runs, Run 4's final concentration was found to be 3871 mg/L and that of Run 6 to be 7980 mg/L. These results illustrate that a higher initial sweep concentration favours a higher final aluminium concentration. Moreover, it demonstrates that the hydrodynamic effect is smaller in relation to the ability of the acid to draw aluminium ions to the sweep via ionic exchange. This however is not to say the hydrodynamic effect is not significant. This is seen at a period around 25-28 hours (transition from Donnan equilibrium to osmotic transport zone) where most of the runs sweep aluminium ion concentration on average slowly tapers off until the end of the run. Given this, it would be prudent to have a future investigation at much lower acid concentrations in order to see if the hydrodynamic transport phenomenon can be mitigating and thus increase the final concentration of aluminium.

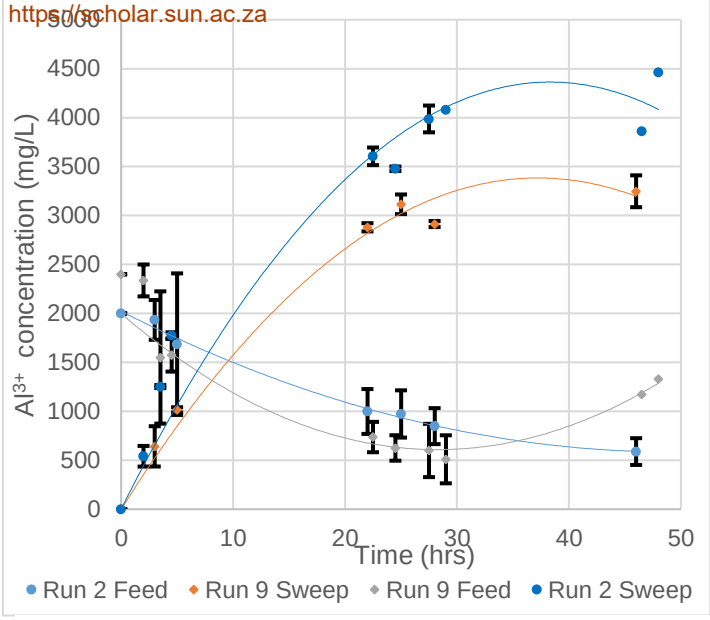
Runs 1 and 6 differ by about 1645mg/L and yet they both were run with the same feed concentrations and sweep concentrations. Similarly Runs 3 and 4 were also run with the same feed and sweep concentration and yet they differ by about 1079 mg/L. This difference of at least 1000 mg/L of aluminium indicates that feed flow rate and/or sweep flow rate also play an important role in aluminium transfer and transport. Those are the only two factors that differentiate the runs. Consequently, the effect feed flow rate and sweep flow rate has on aluminium transport and the final concentration will be investigated in the next section.

4.4.4: Effect of feed flow

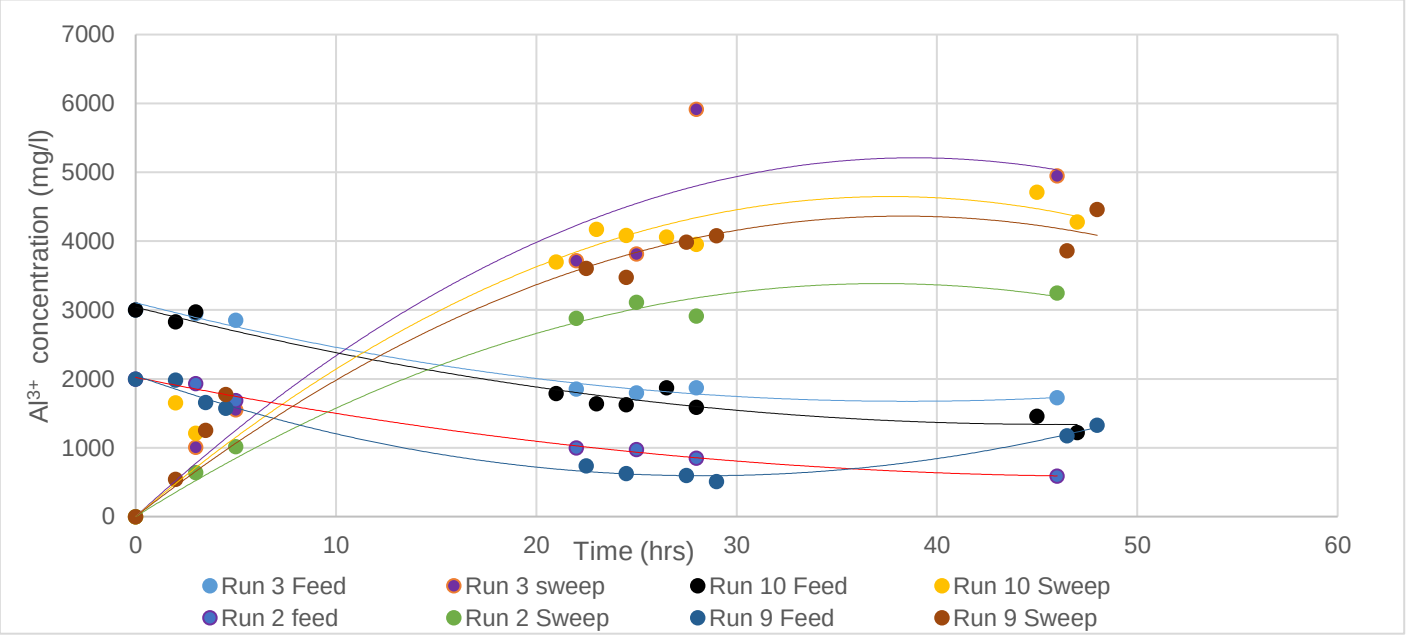
The effect of flow rate was investigated with run pairs 3 and 10 as well as 2 and 9. For Runs 3 and 10, the feed concentration was held constant at 3000 mg/L, sweep concentration at 1M and sweep flow rate at 2.2 mL/s. The feed flow rate was varied from 2.2 mL/s (Run 3) to 4.9 mL/s (Run 10). Runs 2 and 9 were operated at a feed concentration of 2000 mg/L, 1M sweep concentration and 4.9 mL/s sweep flow rate. Feed flow was varied from 2.2 mL/s (Run 9) to 4.9 mL/s (Run 2). The results are displayed in Figure 4-10.



(A) High initial feed concentration, low sweep acid concentration, low sweep flow rates, and varying feed flow rate



(B) Low initial feed concentration, low sweep acid concentration, high sweep flow rate, and varying feed flow rate



(C) Comparison of all runs conducted for the effect of feed flowrate on final aluminium ion concentration

Run	Conditions(feed conc, sweep conc, feed flow rate, sweep flow rate)
3	3000 mg/L 1M 2.2 mL/s ,2.2 mL/s
10	3000 mg/L 1M 4.9 mL/s, 2.2 mL/s
9	2000 mg/L 1M 4.9 mL/s, 4.9 mL/s
2	2000 mg/L 1 M 2.2 mL/s, 4.9 mL/s

Figure 4-10: Effect of feed flow rate at constant feed concentration, sweep concentration and sweep flow rate. Trend lines added for visual clarity.

Figure 4-10A displays the trends of the feed and sweep concentrations of Runs 3 and 10. Starting off with the sweep of Run 3, it can be seen that in 5 hrs of operation, the sweep side obtains a concentration of 1800 mg/L. From 5 hrs until 28 hrs the sweep further increases by 4118 mg/L to a maximum concentration of 5918 mg/L. Then in the last 18 hours of operation, the final concentration which is obtained decreases to 4950 mg/L. looking at the sweep concentration of Run 10, after the first 3 hours of operation the concentration can be seen to increase by 1800 mg/L as well. From 3 hrs to 23 hrs the concentration increases to 4173 mg/L. From 23 hrs until the end of the experiment the concentration of the sweep then increases slightly to 4280 mg/L.

The sweep concentrations of run pair 3 and 10 differ by about 700 mg/L, with Run 3 having the higher final concentration. This result indicates that a lower feed flow rate provides a higher final sweep concentration of aluminium. Moreover, from the difference of 700 mg/L it highlights that the effect of feed flow rate on the final sweep concentration of aluminum is quite significant. Baker (2013) investigated the effects of flow rate on membrane systems. He found polarization to happen when a gradient occurred at the membrane and solution interface due to the selective transport of certain species faster than others. Baker (2013) found that creating turbulence in the system by either increasing the velocity or via tortuous flow paths drastically increased the rate of transport of species from one side of the membrane to the other. In the case of aluminium and this investigation however, the opposite was found to be true. Decreasing the flow rate was found to favour a higher final concentration of aluminium in the sweep side. The Reynolds numbers for both runs were calculated using flow over a flat plate geometry. The Reynolds numbers were found to be 9400 and 21000 respectively, indicating both flows to be laminar (transition number from laminar to turbulent flow is 500,000 for flat plate geometry). It is currently unclear as to why the behaviour of the flow rate goes against findings from literature.

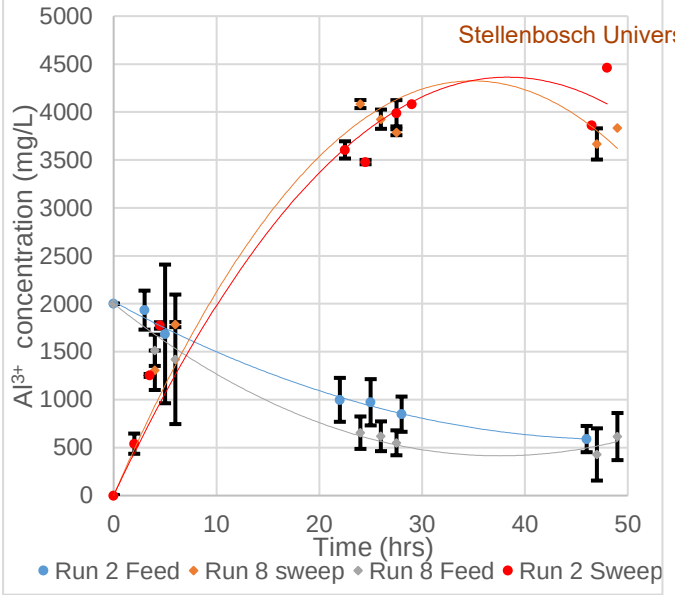
Figure 4-10B compares Runs 2 and 9. From inspection of the sweep of Run 9 it can be seen that for the first 5 hours of investigation (kinetic zone) Run 9 reaches a sweep concentration of 1015 mg/L. The concentration continues to rise for the next 20 hours and at 25 hours (Donnan equilibrium zone) into the investigation reaches 3115 mg/L. From here (osmotic transport zone), the concentration increases slightly until the end of the investigation where it reaches a final value of 3248 mg/L. The trend of the sweep of Run 2 is similar. After 5 hours of operation (kinetic zone) Run 2 reaches a concentration of 1774 mg/L. At 29 hours into the experiment, the final Donnan equilibrium concentration was found to be 4080 mg/L. By the end of the investigation, the final concentration of Run 2 was found to be 4463 mg/L.

The concentrations of run pair 2 and 9 differ by about 1200 mg/L of aluminium in favour of the lower flow rate. Similarly to Runs 3 and 10, these results also indicate that a lower feed flow rate provides a higher final aluminum sweep. Figure 4-10C compares all of the runs on one graph for convenience.

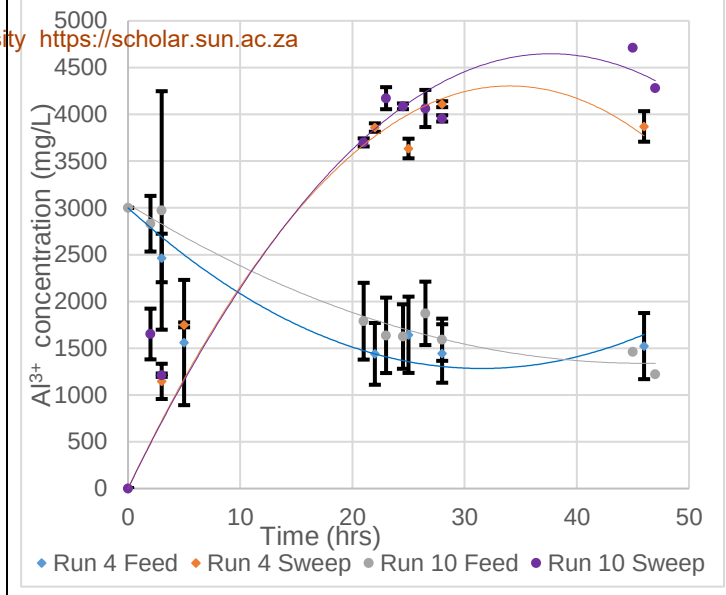
Lastly, as a final note, Runs 2, 9 and 10 serve as proof that the results displayed by the sweep of Run 6 in Figure 4-9B were not anomalous. The sweep concentration of Run 6 was found to be 7503 mg/L at the end of the Donnan equilibrium zone, instead of decreasing as the run went into the osmotic driven zone, the concentration was found to increase to 7980 mg/L by the end of the investigation. Similarly, the sweep concentration of Run 2 was found to be 3115 mg/L at the end of the Donnan equilibrium zone, and then increased to 3248 mg/L by the end of the experiment. Runs 9 and 10 were also found to increase from 4080 mg/L and 4173 mg/L at the end of the Donnan equilibrium zone to 4463 mg/L and 4280 mg/L at the end of the osmotic driven zone respectively. These trends serve to show that using a combination of variables at specific operating conditions can mitigate the effects of osmotic transport towards the end of the investigation. This means that the rate of water transport to the sweep can be made smaller than the rate of transport of aluminium to the sweep, thus increasing the overall aluminium concentration in the sweep. The specifics of this will be investigated further in the optimization section.

4.4.5: Effect of sweep flow rate

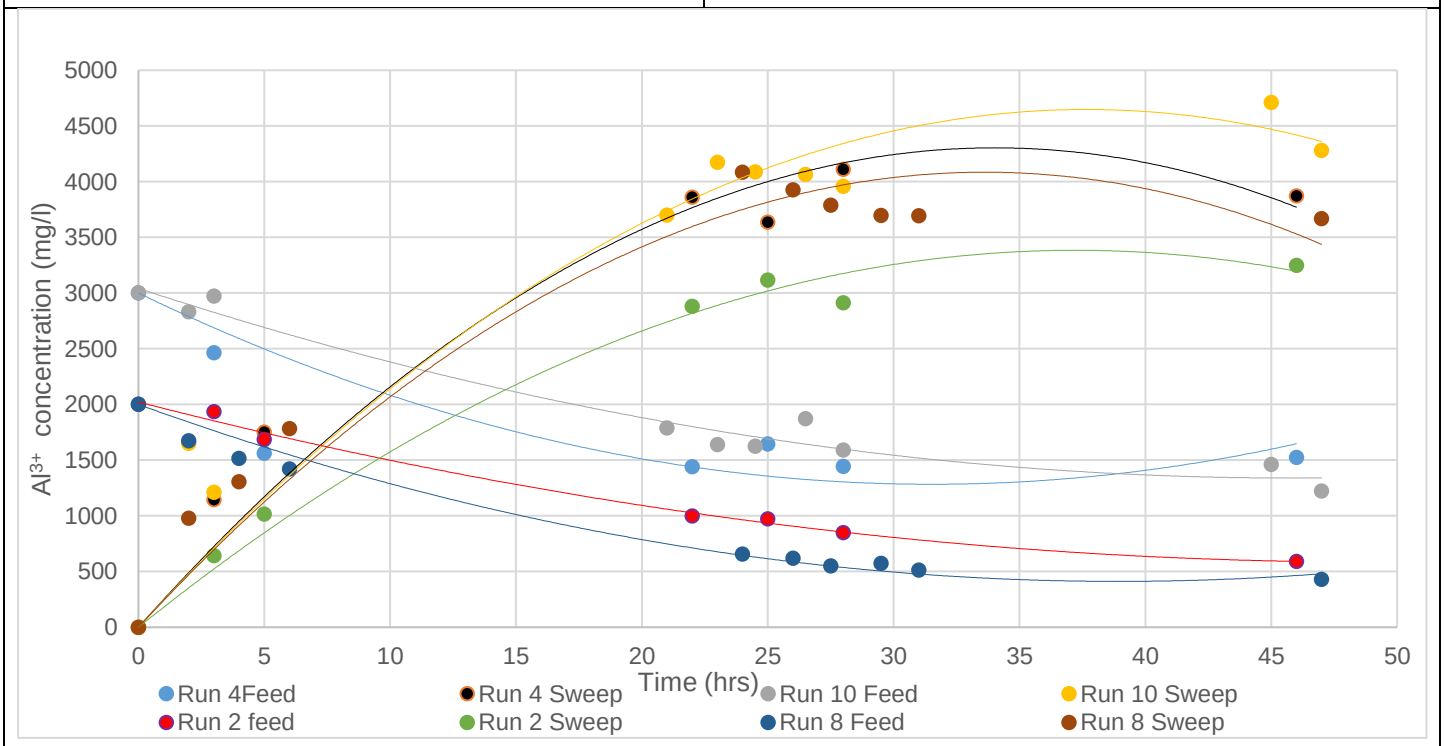
The last variable, sweep flow rate was then investigated in order to determine its relationship with the final aluminium ion concentration recovered in the sweep side. For the investigation, run pairs 10 and 4 as well as 8 and 2 were utilized. Runs 4 and 10 were operated at a feed concentration of 3000 mg/L, sweep concentration of 1M, feed flow rate of 4.9 mL/s. The sweep flow rate was varied from 2.2 mL/s (Run 10) to 4.9 mL/s (Run 4). Runs 2 and 8 were operated at a feed concentration of 2000 mg/L, 1M sweep concentration and 4.9 mL/s feed flow rate. Similarly, the sweep flow rate was varied from 2.2 mL/s (Run 8) to 4.9 mL/s (Run 2). The results obtained are displayed with the aid of the Figure 4-11.



(A) Low initial feed concentration, low sweep acid concentration, high feed flow rate, and varying sweep flow rate



(B) High initial feed concentration, low sweep acid concentration, high feed flow rate, and varying sweep flow rate



(C) Comparison of all runs conducted for the effect of sweep flowrate on final aluminium ion concentration

Run	Conditions(feed conc, sweep conc, feed flow, sweep flow)
2	2000 mg/L 1M 4.9 mL/s, 4.9 mL/s
8	2000 mg/L 1M 4.9 mL/s, 2.2 mL/s
10	3000mg/L 1M 4.9 mL/s, 2.2 mL/s
4	3000mg/L 1M 4.9 mL/s, 4.9 mL/s

Figure 4-11: Effect sweep flow rate at constant feed concentration, sweep concentration and feed flow rate. Trend lines added for visual clarity.

Figure 4-11A compares Runs 2 and 8. From inspection of the sweep of Run 8 it can be seen that: for the first 6 hours of investigation Run 8 reaches a sweep concentration of 1783 mg/L. The concentration continues to rise for the next 18 hours and at 24 hours into the investigation reaches a maximum of 4083 mg/L. After this, the concentration decreases until the end of the investigation where it reaches a final value of 3667 mg/L. The trend of the sweep of Run 2 is similar. After 5 hours of operation Run 2 reaches a concentration of 1015 mg/L, the maximum concentration is reached 25 hours into the experiment and was found to be 3115 mg/L. By the end of the investigation, the final concentration of Run 2 was found to be 3248 mg/L. As with the graphs investigating feed concentration, sweep concentration and feed flow rate, the figure can be divided into the three zones as well, namely, the kinetically driven zone from 0-6 hours, the Donnan equilibrium zone from 6-25 hours, and the osmosis driven zone from 25 hours onward.

From Runs 2 and 8 it would seem that a lower sweep flow rate yielded a higher final aluminium concentration in the sweep. However, looking at the general trend and overlap of the error bars in the feed and sweep profiles of Runs 2 and 8, the overlapping error bars illustrate that it is possible there is no difference in the results of the two runs.

Figure 4-11B further investigates the effect of sweep flow rate with the use of Runs 4 and 10. Looking at the sweep concentration of Run 10, after the first 3 hours of operation the concentration can be seen to be 1800 mg/L. From 3 hrs to 23 hrs the concentration increases to 4173 mg/L. At 23 hrs until the end of the experiment the concentration of the sweep then increases slightly to 4280 mg/L. In terms of the sweep of Run 4, the kinetically driven zone (0-5 hrs.) yielded an aluminium concentration of 1750mg/L, the Donnan equilibrium zone (5-28 hrs) was found to further concentrate aluminium ions to a maximum concentration of 4109 mg/L. The osmosis driven zone (28-46hrs) was found to dilute the aluminium concentration in the sweep to a final value of 3871 mg/L.

Similarly to Runs 2 and 8, the general trend of the overlapping error bars in most of the time intervals suggested there is no difference in results from the experiments performed.

Run pairs 10 and 4 as well as Runs 2 and 8 which investigated the effect of sweep flow rate were found to differ by about 409 and 419 mg/L respectively. Run pairs 2 and 4 as well as 1 and 5 which investigated the effect of feed concentration were found to differ by 623 mg/L and 3754 mg/L respectively. The investigation of the effect of feed flow rate utilized run pairs 2 and 9 as well as 3 and 10. The aluminium sweep concentration differences of each pair were found to be 670 mg/L and 1215 mg/L respectively. Lastly the investigation on the effect of sweep concentration on the final aluminum concentration in the sweep made use of run pairs 1 and 3 as well as 4 and 6. The final concentration differences of the pairs were found to be 1385 mg/L and 4109 mg/L. Looking at these values it is evident that the effect of varying sweep flow rate on the final aluminium concentration is the least significant as the final concentration differences between each pair is not as large (this is in addition to the error bars suggesting there is no difference in the runs performed). The other investigations of the effects yielded concentration differences of at least a magnitude (looking at the largest difference in the pairs) in difference compared to the effect of sweep flow rate. Putting this into percentages. Using the largest concentration difference of the pairs: the effect of varying sweep flow rate only produced 11% $(100 * \frac{419}{3754})$ of the difference in varying the feed concentration. Similarly, when comparing the sweep flow rate to the effect of varying sweep concentration, the effect of varying sweep flow rate only produced 10% $(100 * \frac{419}{4109})$ of the effect of varying the sweep concentration. Lastly, when comparing varying the sweep flow rate to the effect of varying the feed flow rate had on the final aluminium concentration, the sweep flow rate yielded 34% $(100 * \frac{419}{1215})$ of the effect of varing the feed flow rate. Given this, the effect of varying the sweep flow rate was found to be the least significant parameter towards increasing the final aluminium concentration in the sweep.

4.4.6: Summary

To summarize this section, an investigation to determine the effects of feed concentration, sweep concentration, feed flow rate and sweep flow rate on the concentration of aluminium in the sweep was carried out. A full factorial design with two levels was used to assess this. The feed at 2000 mg/L and 3000 mg/L of aluminium, the sweep at 1M and 2 M HCl as well as feed and sweep flow rates at 2.2 mL/s and 4.9 mL/s. The experimental runtime of 46- 48 hours was selected with guidance from literature.

The effect of sweep flow rate was found to have the least significant effect on the final aluminium ion concentration in the sweep.

The effect of sweep concentration was found to be a combination of two factors. Firstly, a higher sweep concentration was found to increase the volume of water transported across to the sweep side and hence dilute the concentration of aluminium ions recovered. Secondly, a higher sweep concentration was found to provide a higher electrochemical potential which resulted in a higher transport of aluminium ions to the sweep. The results obtained demonstrated that the hydrodynamic effect was found to be smaller in relation to the ability of the acid to draw aluminium ions to the sweep via ionic exchange.

Lastly, the trend of the feed concentration was found to also be a function of the sweep acid concentration. A higher concentration of aluminium was recovered in the sweep for high feed concentrations only when high acid sweep concentrations were used. A higher aluminium concentration was recovered in the sweep using low feed concentration when low acid sweep concentrations were used.

4.5: Optimization of the Donnan Dialysis Process

4.5.1: Introduction

This section focuses on a final set of experiments incorporating the information that was learnt from the investigations performed in section 4.4. The objectives of this section are as follows:

1.) Reduce acid sweep concentrations levels to mitigate water transport from the feed to the sweep side.

2.) Range acid sweep concentration levels from 0.25 M to 0.75M in order to make the process more feasible for industrial use (running at 2M requires special piping and safety procedures to be put in place, which leads to higher expenses)

3.) Running the feed at a different band of feed concentrations and investigate this effect on the recovery of aluminium. This is because, while feed concentration is a variable, it cannot be controlled as it comes from water treatment residuals and may differ from plant to plant.

4.) Manipulating feed concentration, sweep concentration and feed flow rate in order to try and reach the highest recoveries in the process.

5.) Eliminating sweep flow rate as a variable as this was found to be the least significant variable.

6) Increasing the number of levels for each parameter being investigated in order to get a more accurate view of the process.

The section is divided into two parts. The first part consists of the modelling and optimization of the process which results in the derivation of a statistical model. The model was calculated from the results of experiments conducted using a Box Behnken design. The Box Behnken design was used because it utilized three factors at three different levels to evaluate the relationship between variables and their effects using only 15 runs. In addition, the three levels make it possible for model development through least squares regression. The curvature the three levels provide in model development makes it possible to represent the responses of the variables using Response Surface Methodology (RSM). The coded values and factors used may be seen in Table 4-5 and 4-6. The second section utilizes the statistical model calculated to design response surface methodology plots for the effects of feed concentration, sweep concentration and feed flow rate. The response factor was chosen as aluminium recovery as the experiments conducted with the new operating conditions were found to greatly reduce water transport to the sweep to about 20 mL, hence using concentration as a response to monitor water transport was no longer necessary. The recovery at any instant in time (t) was calculated as:

$$Al^{3+}\ recovery\ (t) = \frac{(Sweep\ concentration)(t) * (Sweep\ volume)(t)}{(Inital\ Feed\ concentration) * (Initial\ feed\ volume)} \qquad \text{Equation 4-2}$$

4.5.2: Selection of 'Real' operating conditions and Design of experiments

The previous chapter which performed investigative runs on the four chosen variables: feed flow rate, sweep flow rate, feed concentration and sweep concentration utilized operating conditions similar to that of literature.

In terms of industrial applications however, it is highly impractical to operate at acidic concentrations of 1 M and 2 M. This would require extremely expensive equipment and have very high safety risks. Concentration ranges of 0.2 M to 0.8 M were found to be more feasible and practical for use in a municipal potable water treatment plant (Tredoux, 2016). Moreover, in terms of the Water Treatment Residual (WTR) concentrations, Tredoux (2016) cited that ranges of 200 mg/L to 800 mg/L were to be expected.

This section investigates these recommendations for use in a municipal potable water treatment plant. Tables 4-5 and 4-6 show the design of experiments as well as the levels of the factors used utilizing the Box Behnken design for this investigation.

Table 4-5: Box Behnken design

	Codes		
Test no	Flow rate	Aluminium feed Conc	Acid sweep Conc
1	-1	-1	0
2	1	-1	0
3	0	0	0
4	-1	1	0
5	1	1	0
6	-1	0	-1
7	1	0	-1
8	0	0	0
9	-1	0	1
10	1	0	1
11	0	-1	-1
12	0	1	-1
13	0	-1	1
14	0	1	1
15	0	0	0

Table 4-6: Table of factors for Box Behnken

Condition	Symbol	Flow rate	Aluminium feed conc	Acid sweep conc
Low	-1	3.5 mL/s	300 mg/L	0.25 M
Medium	0	4.5 mL/s	500 mg/L	0.5 M
High	1	5.5 mL/s	700 mg/L	0.75 M

4.5.3: Statistical modelling

From the Box Behnken design of experiments and recoveries yielded, a statistical model using least squares methods was constructed to represent and model the data. The time dependant data and regression analysis may be seen in Appendix A (tables A-7 to A-13). In matrix form the expression can be written as:

Y=BX+E Equation 4-3

Where Y is the matrix of measured values, X is a vector of independent variables and E is a matrix of coefficient of errors (Tripathy and Rama, 2012). Further expanding this equation results in the below quadratic equation. A second order model with interactive effects was selected in order to accurately depict the response surface and curvature, as well as to accurately represent the interactive process parameters through two and three dimensional responses (Tripathy and Rama, 2012).

$$Y_{recovery} = \beta_1 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} {X_1}^2 + \beta_{22} {X_2}^2 + \beta_{33} {X_3}^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3$$ Equation 4-4

Where β_{ii} coefficients are quadratic coefficients, β_{iJ} are interaction coefficients and β_i are the main effects. These coefficients are found through regression analysis. X_1 Is the feed flow rate, X_2 is the feed concentration and X_3 is the sweep concentration.

The final model calculated using natural variables was found to be in the form of a quadratic function with interaction parameters. The model obtained can be seen below:

$$Y_{recovery} = 2.13 \times 10^2 - 32.7 X_1 - 1.70 \times 10^{-1} X_2 + 28.7 X_3 + 3.40 {X_1}^2 - 78.8 {X_3}^2 + 5.00 \times 10^{-4} X_1 X_2 + 2.40 \times 10^{-1} X_1 X_3 + 1.00 \times 10^{-1} X_2 X_3$$ Equation 4-5

Figure 4-12 below compares the experimental values obtained to those obtained using the model above. A straight line was fitted on to the data and an R^2 value of 0.99 was obtained, indicating that the model predicted the experimental data accurately.

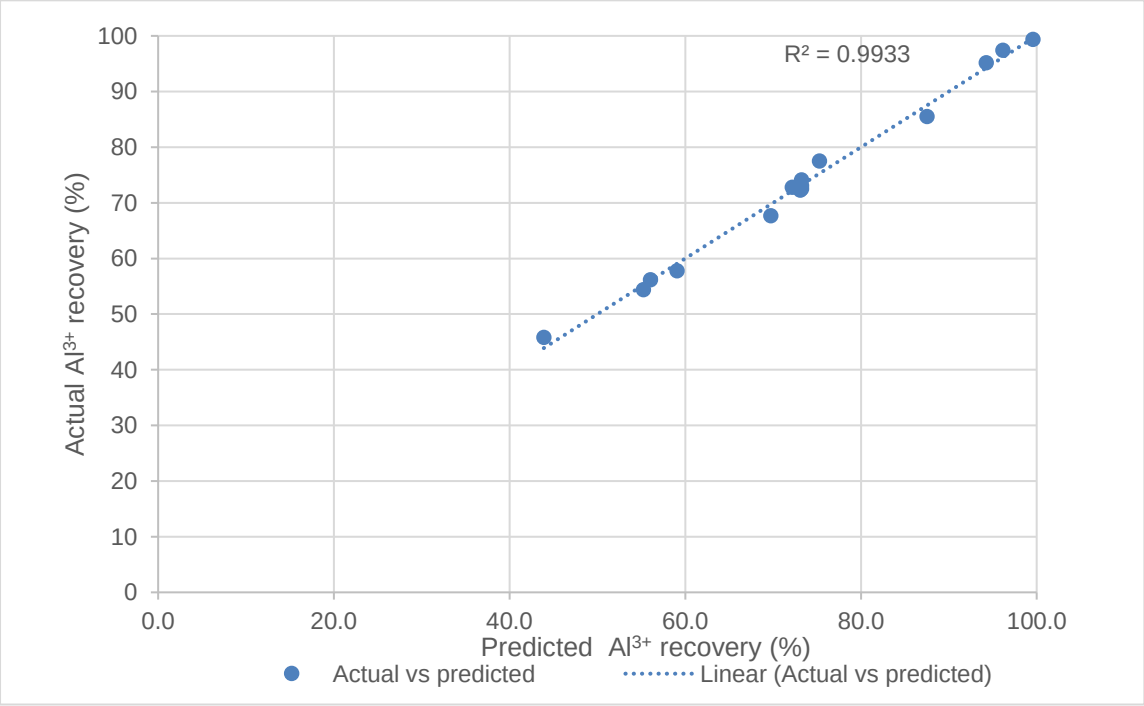


Figure 4-12: Actual vs Predicted recovery

A further step to assess the fit of the model was through the use of a residual plot which can be seen in Figure 4-13. A residual plot is a graph which essentially shows the difference between the observed value of the dependant parameter (in this case recovery) and predicted value (using the model). This difference between the observed and predicted values is called the residuals. The objective of the plot is to make it visually easier to see how far off the predicted data was from the observed.

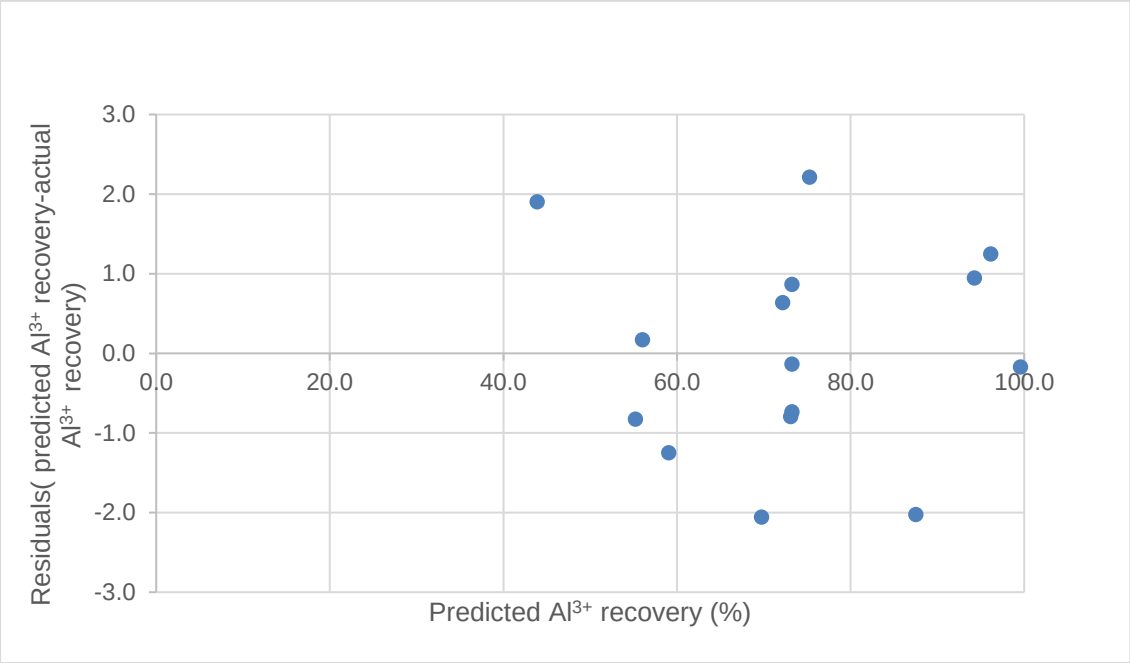


Figure 4-13: Residual plot

A negative residual value indicates that the model over predicts the data, and a positive residual indicates the model under predicts the data. From the residual plot above, the lowest and highest residuals for the data set were found to be -2 and +2.1 with most of the data being quite close to zero (which would indicate perfect fit). Lastly, an F test was used to compare the two data sets in order to see if the model was significant.

According to Montgomery et al. (2013), an F test is used to compare the variances of two populations in hypothesis testing. Simply put, the test uses a ratio of the two populations or sample sets to measure the dispersion and scatter of data from the mean. From this, it can be ascertained whether or not the two sample populations are similar or not. The null hypothesis in an F test states that the variances of the populations are equal, the alternative hypothesis states that the variances are different. In order to accept or reject the null hypothesis, an F statistic is compared to the critical F statistic. If the F statistic is greater than the critical F statistic then the null hypothesis may be rejected.

For this investigation, the experimental data was compared to the predicted data provided by the model. The F critical value was compared to the F value using a confidence interval of 95%. The F critical value was found to be 2.48 and the F value 1.06. Because the F value is lower than the F critical value, it can be concluded that the variances of both data sets are the same and thus the model is statistically significant at a confidence of 95%.

4.5.4: Effect of feed concentration

The statistical model was used to draw surface plots illustrating the effect of feed concentration on aluminium ion recovery. Three plots were drawn, in each plot the aluminium feed concentration was held constant at 300 mg/L, 500 mg/L and 700 mg/L. The results are illustrated in Figure 4-14.

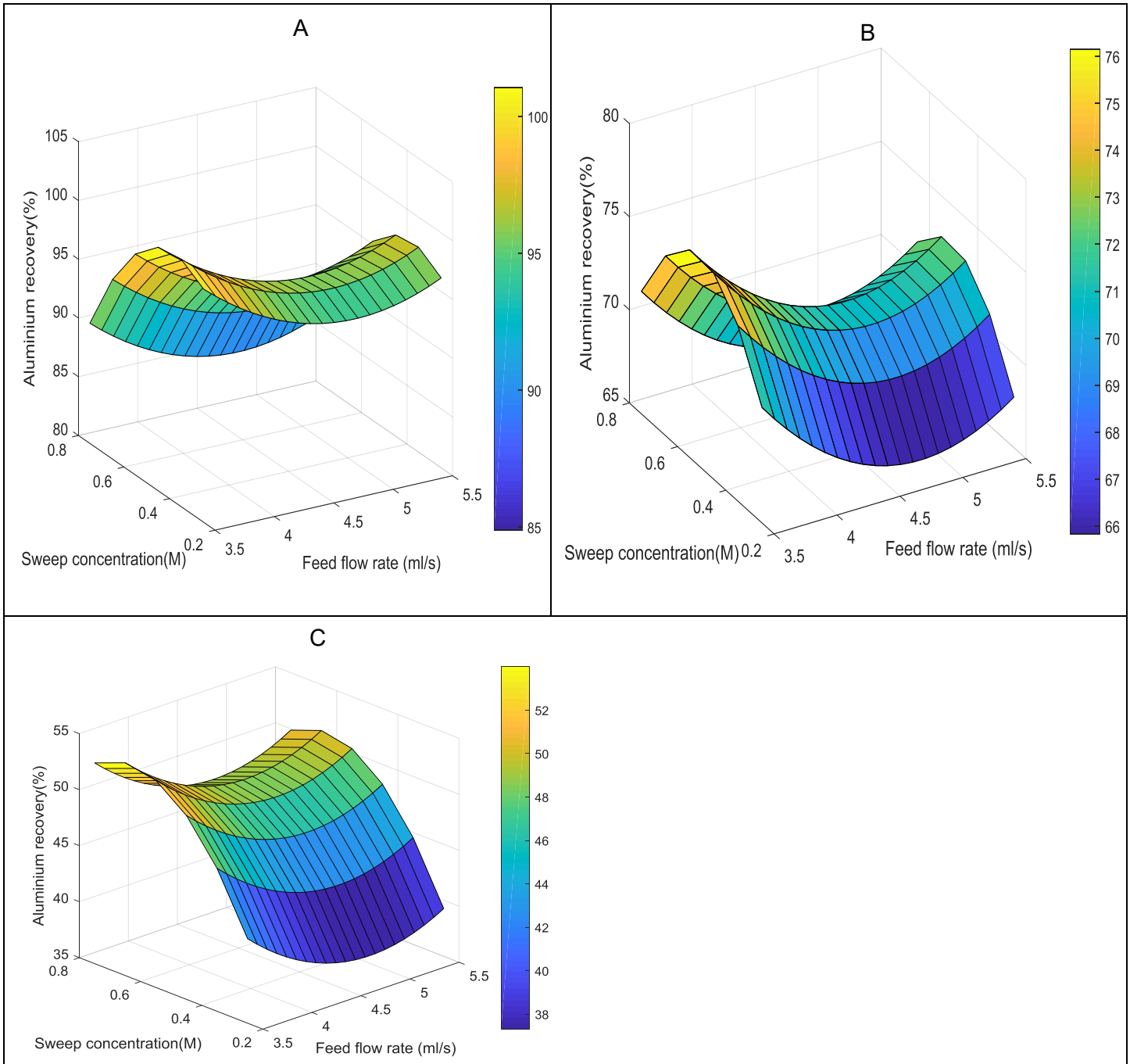


Figure	Feed concentration
A	300 mg/L
B	500 mg/L
C	700 mg/L

Figure4-14: Surface plots of the effect of feed concentration on aluminium ion recovery

Figure 4-14A illustrates the surface plot of aluminium ion recovery when the feed concentration is kept at the lowest (300 mg/L). The aluminium ion recovery was found to range between 85% and 97%. The highest recoveries where found to be when the feed flow was low (3.5-4 mL/s) and the sweep concentration was high (0.6-0.8M). A higher initial acid concentration also means a higher concentration of hydrogen ions present in solution. These ions make it possible for more proton exchange to occur, via the kinetically driven zone and the Donnan equilibrium zone.

The responses of surface plots in Figure 4-14B were calculated at a constant feed concentration of 500 mg/L. The attainable recoveries were found to range between 65% and 72%. Similar to Figure 4-14A, the highest recoveries where found to be when the feed flow was low (3.5-4 mL/s) and the sweep concentration was high (0.6-0.8M).

Lastly Figure 4-14C illustrates the recovery of aluminium ions at a constant feed concentration of 700 mg/L. Aluminium ion recoveries ranged between 35% and 52% with low feed flow rates and high sweep concentration also favouring the high recoveries.

The effect of feed concentration was found to be statistically significant with a p value of 0.00 being obtained at 95% confidence. Looking at Figures 4-14A, B and C it is evident that lower feed concentrations favour a higher aluminium ion recovery. At low feed concentrations there is less mass of aluminium present. Given this, most of the ionic transfer occurs in the electrochemically driven and sometimes Donnan equilibrium zone. By the time the process enters the second and third zones, most if not all of the aluminium has been transferred and used up. In short, the aluminium is used up in the kinetically driven section, which is the section with the fastest rate of recovery of aluminium.

4.5.5: Effect of feed flow rate

Similarly to section 4.5.4, the statistical model calculated and subsequently tested for significance and accuracy in section 4.5.3 was used to draw surface plots illustrating the effect of feed flow rate on aluminium ion recovery. Three plots were drawn, in each plot the aluminium feed flow rate was held constant at 3.5 mL/s, 4.5 mL/s and 5.5 mL/s. The results are illustrated in Figure 4-15.

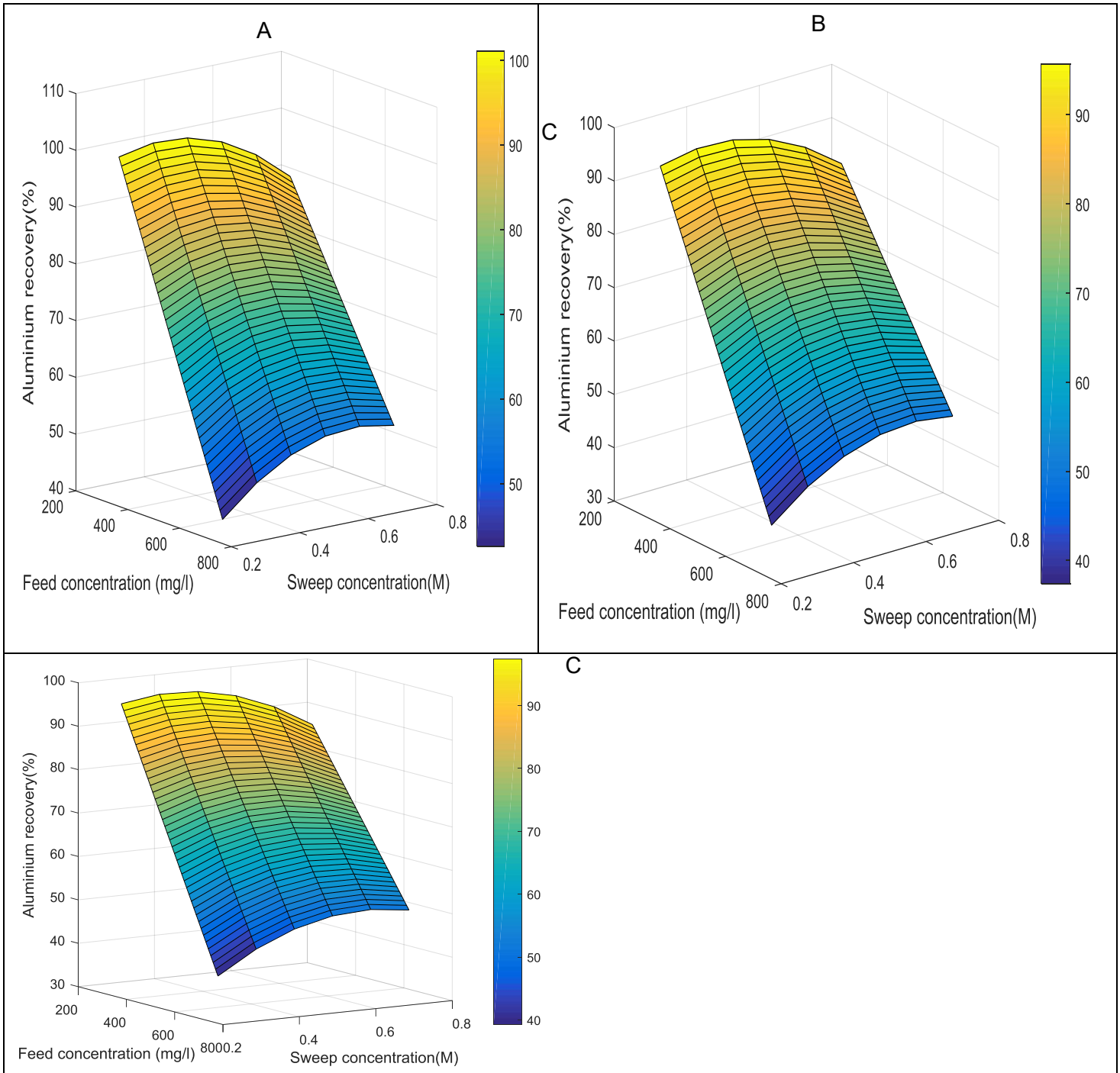


Figure	Feed flowrate
A	3.5 mL/s
B	4.5 mL/s
C	5.5 mL/s

Figure4-15: Surface plots of the effect of feed flow rate on aluminium ion recovery

Figure 4-15 A depicts the ion recovery profile of aluminium as a function of sweep and concentration. The feed flow rate was held constant at 3.5 mL/s. The highest aluminium recoveries were found to occur at medium sweep concentrations (0.4-0.6 M) and low feed concentrations (200 mg/L). The maximum aluminium ion recovery was found to be 98% at these conditions.

Figure 4-15 B illustrates recovery profiles of aluminium when the feed flow rate was held constant at 4.5 mL/s. The highest recovery obtained was found to be 93% medium sweep concentrations and low feed concentrations.

The conditions for which the highest aluminium ion recoveries were obtained when feed flow rate was held constant at 5.5 mL/s in Figure 4-15 C are similar to that of Figure 4-15 A and B. The highest aluminium ion recovery was found to be 97%.

Figures 4-15A, B and C illustrate that varying the feed flow rate does not relate to an increase or decrease in aluminium ion recovery. The maximum ion recoveries in all three feed flow rate scenarios differed by about 4% when other inputs were at their optimal values. The effect of varying feed flow rate was found to be statistically not significant with a p value of 0.31 being obtained at 95% confidence. In addition to this, the recoveries did not necessarily increase or decrease with an increase in flow rate. These results suggest that at the new lower operating conditions selected for modelling and optimization, concentration polarization and external film mass transfer effects are not the rate limiting steps. If they were, then varying feed flow rate and thus increasing mixing and turbulence would have an effect on the recovery of aluminium ions.

4.5.6: Effect of sweep concentration

Figure 4-16 assesses the effect of varying sweep concentration at three different operating conditions of 0.25 M, 0.5M and 0.75 M on the recovery of aluminium ions.

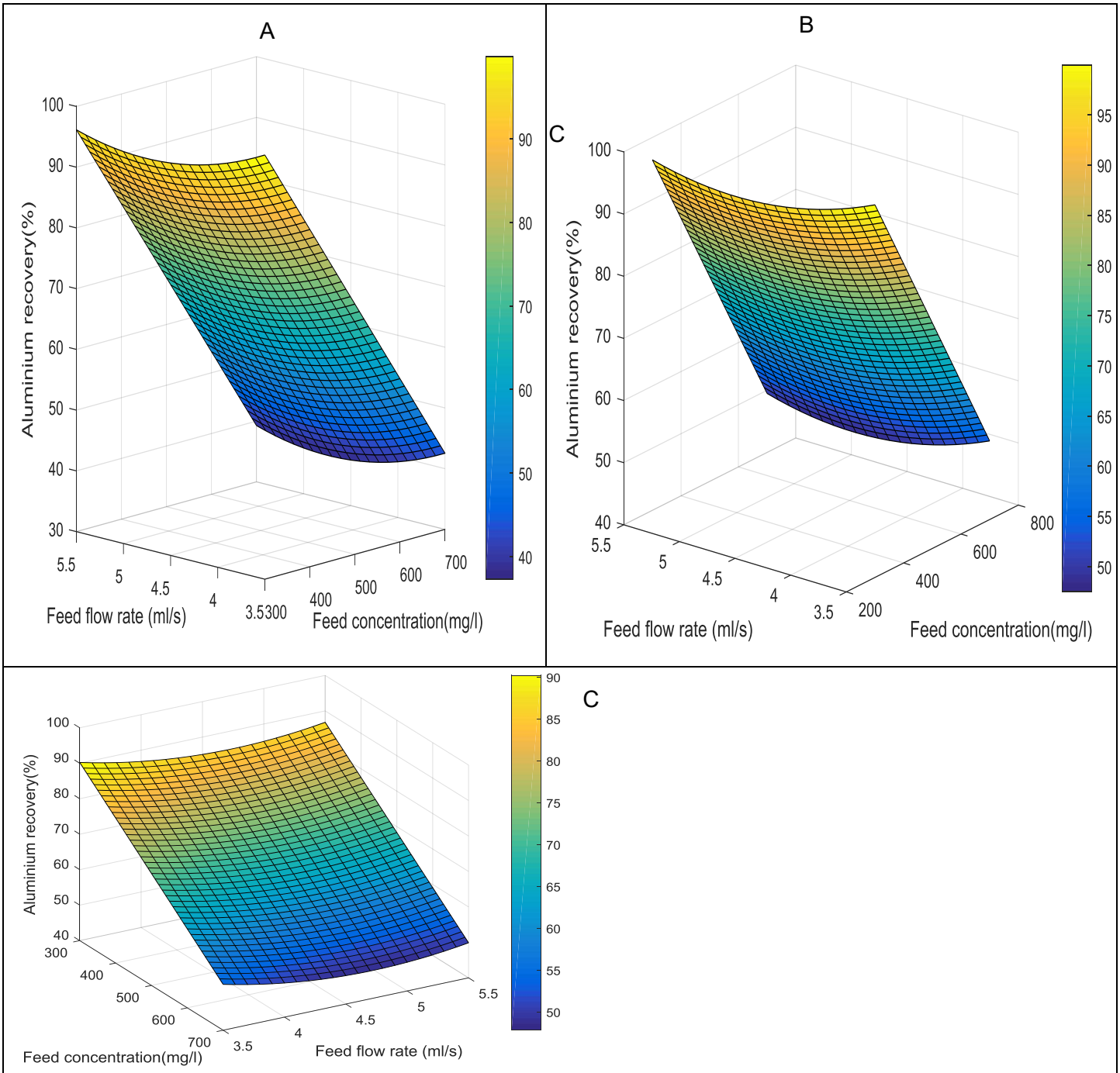


Figure	Sweep concentration
A	0.25 M
B	0.5 M
C	0.75 M

Figure 4-16: Surface plots of the effect of sweep concentration on aluminium ion recovery

Figure 4-16A represents the recovery profile of aluminium ions when feed flow rate and feed concentration are varied. The sweep concentration was held constant 0.25 M. the highest recovery obtained was found to be 96%. Varying the feed flow rate was found to have no effect on the recovery, however low feed concentrations (300 mg/L) were found to yield the highest recoveries.

Figure 4-16B represents a surface plot conducted at a sweep concentration of 0.5 M. The highest recovery was found to be 98%. Similarly to the surface plots illustrated at a sweep concentration of 0.25 M, low feed concentrations were found to yield the highest aluminium ion recovery and feed flow rates were found to have no significant effect

The lowest recoveries were found to be at investigations conducted at a sweep concentration of 0.75M. The highest aluminium ion recovery in the investigation was found to be 90%. The surface plots may be seen in Figure 4-16C.

From the response surface plots of the recovery of aluminium illustrated in Figure 4-16, it can be seen that there is a marginal difference in the highest aluminium ion recoveries obtainable when varying sweep concentration. Statistically, the effect of varying sweep concentration was found to be not significant with a p value of 0.375 being obtained at 95% confidence .Looking at Figure 4-16, the highest recovery was found to be 98%, it was found operating under medium sweep concentrations (0.5 M). In the previous section (section 4.4) it was discussed that operating at higher sweep conditions favoured the mass transfer of aluminium from the feed to the sweep side. This was found to be the ideal operating condition for recovering the highest mass of aluminium ions, however in terms of the final concentration achievable, operating at high sweep concentrations was not favourable because of water transport. In summary it was found that when dealing with concentration, the effect the initial sweep concentration had on the final concentration of aluminium weighed on two factors. The first was that higher acid sweep concentrations caused a higher volume of water to be transferred from the feed to the sweep side. The second factor was that a higher initial sweep concentration caused more mass transfer of aluminium from the feed to the sweep side. From the new operating conditions selected, laboratory scale experiments performed (using Box Behnken design) also showed that the volume of water transported from the feed to the sweep side was found to be greatly reduced, and on average only about 20 mL reported to the sweep.

Due to the great reduction in water transport, if required higher sweep concentrations could be used to increase both the concentration and the recovery of aluminium ions.

4.5.7: Summary

A statistical model was calculated using natural variables. It was found to be of a quadratic nature with interactions. The model can be see below:

$$Y_{recovery} = 2.13 \times 10^{2} - 32.7X_1 - 1.70 \times 10^{-1}X_2 + 28.7X_3 + 3.40{X_1}^2 - 78.8{X_3}^2 + 5.00 \times 10^{-4}X_1X_2 + 2.40 \times 10^{-1}X_1X_3 + 1.00 \times 10^{-1}X_2X_3 \qquad \text{Equation 4-6}$$

In order to test the models significance and accuracy, the predicted data was plotted against the actual data and a straight line was fitted through. An R^2 value of 0.99 was found, indicating the similarity of the predicted data to the actual experimental data. Subsequently, an F test was used in order to assess the significance of the model at a confidence interval of 95%. The F critical value was found to be 2.48 and the F value 1.06. Since the F value was found to be lower than the F critical, the model was found to be significant. From this, response surface plots investigating the effects of feed concentration, feed flow rate and sweep concentration on aluminium ion recovery were drawn.

In summary, from the modelling and optimization results as well as response surface plots, it was found that a combination of low feed concentrations and moderate acid concentrations

were found to yield the highest recoveries of aluminium. The effects of the feed flow rate were found not to be as significant at optimal conditions of sweep and feed concentrations.

In terms of statistical analysis at a confidence interval of 95%, feed concentration was found to be the most significant parameter, the p value was found to be 0.00. Both sweep concentration and feed flow rate were found to be statistically insignificant with p values of 0.375 and 0.301 respectively.

Typically in industry and for Water Treatment Residuals, the feed concentration would be fixed and the two variables to be manipulated would be the feed flow rate and the sweep concentration.

The highest recoveries in the three sections investigating the effect of feed concentration, effect of feed flow rate and effect of sweep concentration were found to be 97%, 98% and 98% respectively. In addition to this, the new operating conditions were found to greatly reduce the transfer of water to the sweep to 20 mL.

4.6: Performance of real water treatment residuals feed

4.6.1: Introduction

Water treatment residuals were obtained in the form of sludge from the Blackheath water treatment plant in the Western Cape. The aim of obtaining this sludge was to determine if organics indeed were unable to penetrate the membrane from the feed to the sweep side. The second objective was to investigate if it was in fact possible to obtain aluminium recoveries as high as those obtained with the synthetic mixtures used in previous experimentation.

4.6.2: Feed preparation

Water treatment residuals were obtained in sludge form from evaporation ponds and HCl acid digestion was consequently done prior to Al^{3+} recovery. The feed digestion procedure is discussed in section 3.6.

Typically on a municipal potable water treatment plant, the stream that would have been used to recover Al^{3+} would have been the stream coming from the settling tanks after flocculation and coagulation has occurred. Due to the infrastructure and design of the Blackheath water treatment plant, this was not possible, hence the use of sludge from evaporation ponds.

The reasoning behind having two digestive solutions differing by an order of magnitude was to determine two effects. Firstly, if increasing or decreasing acid concentration had an effect on the amount of organics and aluminium released from the sludge into solution. Secondly, if the acid concentration affected the kinetics and recovery of aluminium, as well as rejection of organics in the Donnan Dialysis experiment.

4.6.3: Findings

Both feed solutions were operated at 4.5 mL/s feed flow and sweep flow rates. The sweep solution consisted of 1L of 0.5M HCl. Figure 4-17 shows the feed solution after digestion and before experimentation took place. Its dark brownish colour is indicative of a high concentration of dissolved organics.

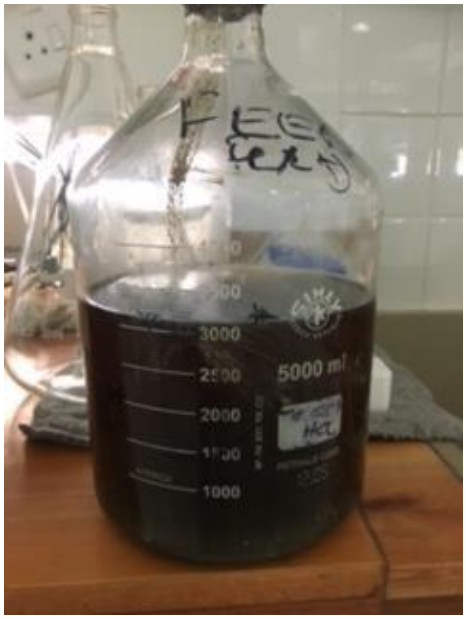


Figure4-17: Digested organic feed before filtration and Donnan Dialysis

Figure 4-18 shows the feed and sweep solutions after 48 hours of Donnan Dialysis run time. The left hand side of the figure shows the feed and sweep solutions of the 0.5M acid digestion process, while the figure on the right is for the 0.05M digestion.

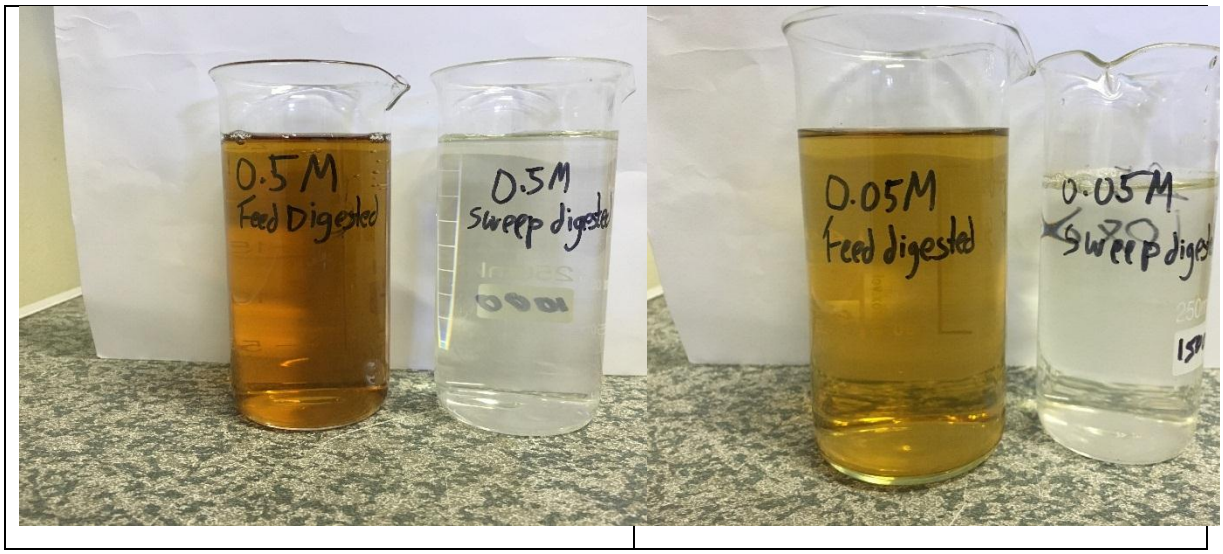


Figure 4-18: Organics at the end of the 48 h dialysis run

The feed side was found to still be a dark brown colour and the sweep side was unchanged in its transparent colour for both of the digestion processes.

4.6.4: Effect of organics

A UV analyser was used and set at wavelength of 254 nm in order to try and determine if any organics from the feed were transferred into the sweep side. UV analysis does not give absolute quantities, but rather relative changes in concentrations of organics. Figure 4-19 provides the results for both the 0.5 M and 0.05 M HCl feeds.

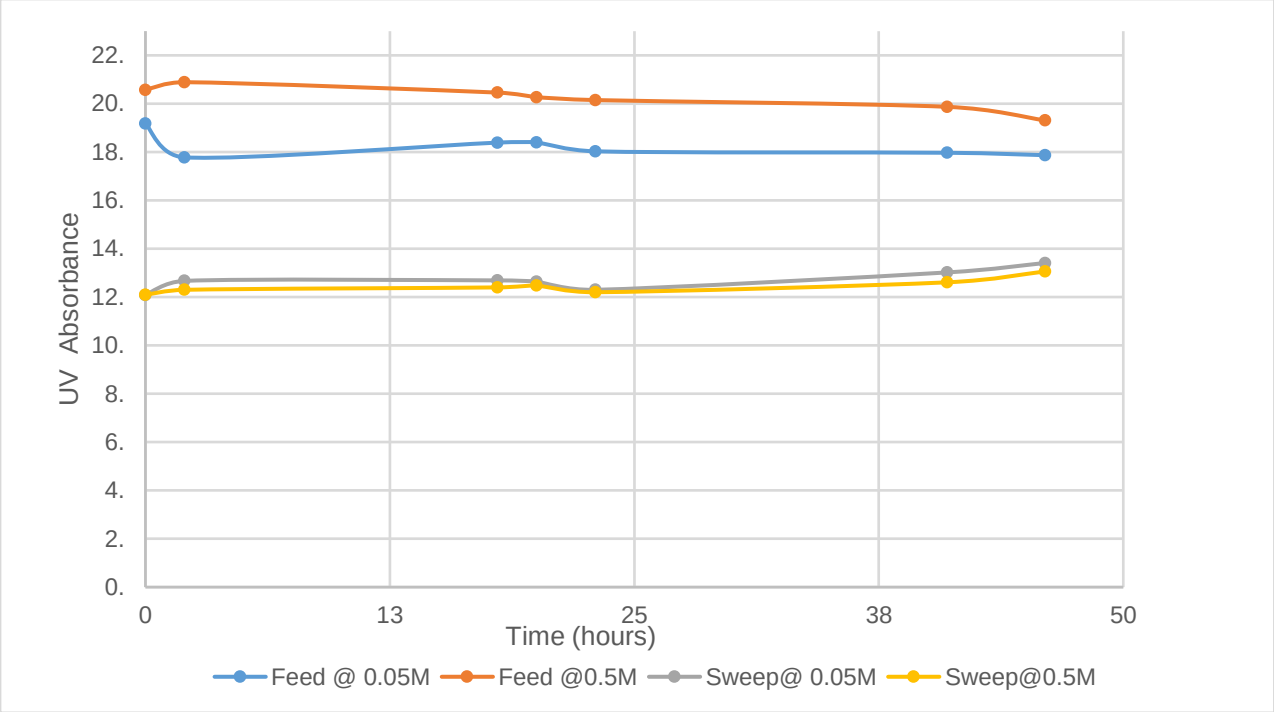


Figure 4-19: UV analysis of organics for 0.5 M and 0.05 M acid sludge digestions

Firstly, the difference in absorbance of the two feeds indicates that a higher concentration of acid was able to breakdown the sludge more successfully, as more organics were found to be in solution. This is seen as the starting absorbance for the 0.5 M feed is 20.6 abs/cm and that of 0.05M is 19.2 abs/cm. The sweep absorbances were however the same as at the beginning as there were no organics present in solution. The reason the absorbance reading was 12 abs/cm and not 0 abs/cm for both sweeps is that the UV254 nm wavelength doesn't just pick up humics and cyclic organics, but other compounds as well. However, our only interest is the organics and hence 12 abs/cm can be taken as a concentration of zero as there are no organics present.

By the end of the run it can be seen that there is a slight decrease in absorbance of the feed and a slight increase in the sweep. This signifies that some organic transportation to the sweep took place. The 0.5M feed started at 20.6 abs/cm and ended up at 19.3 abs/cm indicating that about 6% of organics were transported from the feed to the sweep. Most of this transport can be seen to take place from 40 hours. If the experiment were to be stopped at the 40 hours mark, only 3.4% of organics would be transported. The decision of whether or not to stop at 40 hours hinges on the profile of the recovery of the aluminium which will be discussed in the next section. The 0.05M feed was found to also have a similar value of 6.8% of organic transport, however the 40 hours mark was found not to be as crucial as that of the 0.5M.

4.6.5: Concentrations in Water treatment sample

Lastly, the Atomic Absorption Spectrophotometer was used to analyse the aluminium concentrations of both the sludges digested at 0.5M and 0.05M as well as the Donnan Dialysis runs performed on both these feeds. The total aluminium which was able to be extracted from the sludge into solution was found to be 600 mg/L for the 0.5M HCl digestion and 300mg/L for the 0.05M digestion. These findings corroborate those found with organics in the previous section stating that a higher acid concentration works better at breaking the sludge matrices and thus releasing more organics and aluminium into solution. For the specific case of concentration, it would seem that a change in magnitude of acid concentration results in the doubling of aluminium released into solution. Figure 4-20 illustrates the concentration of aluminium in the feed with time as the Donnan Dialysis investigation was conducted. Trend lines have been used to illustrate the general form of the data.

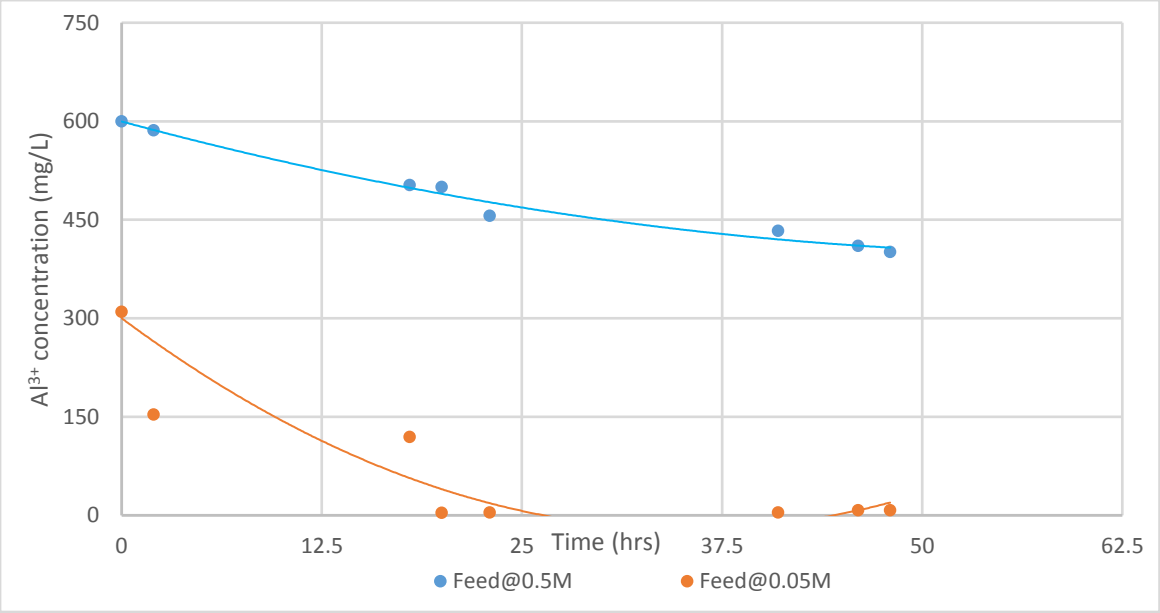


Figure 4-20: Feed concentrations in real WTR

Even though the 0.5M digested feed solution starts off at a higher concentration of 600 mg/L, the final concentration the feed ends off at is still more than half (402 mg/L) of what it was originally. The 0.05M digested feed starts off at a much lower concentration (300 mg/L) unlike the 0.5M feed, however most of the aluminium is transported to the feed side. Figure 4-21 below makes this much clearer by providing this in terms of recoveries. Once again, Trend lines have been used to illustrate the general form of the data.

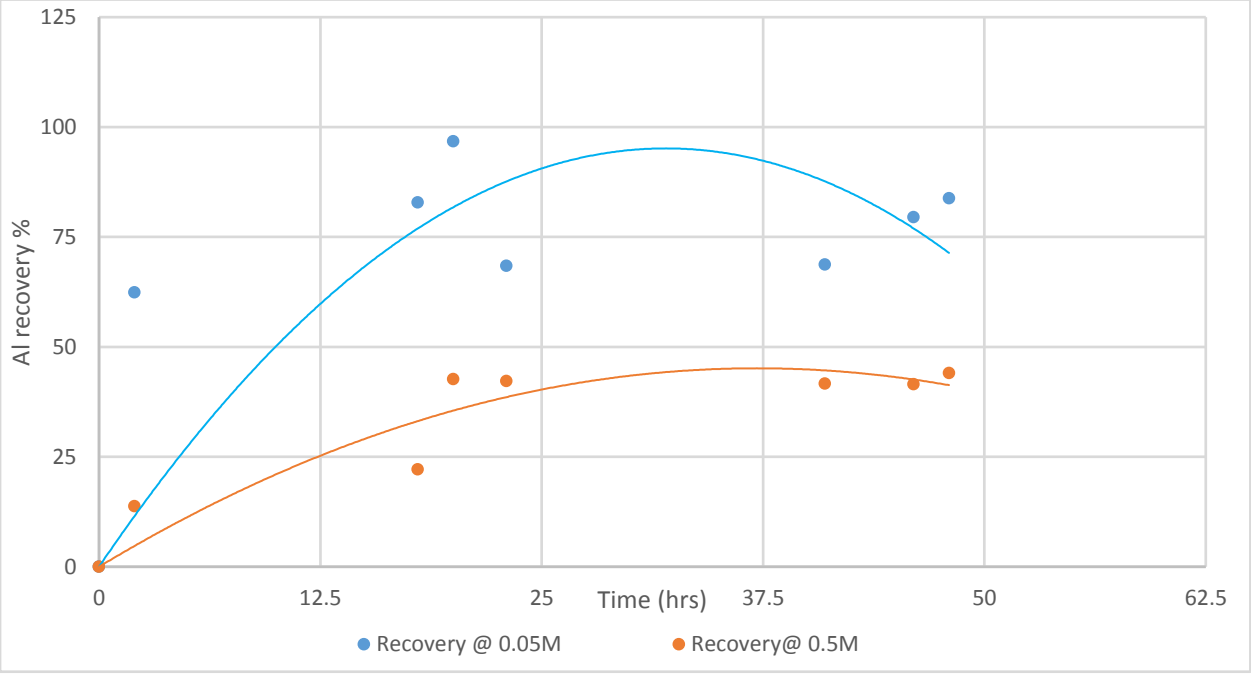


Figure 4-21: Recoveries of WTR

The final aluminium recovery of the 0.5M digested sludge was found to be 44% while that of the 0.05M digested sludge was 84%, almost double. The reason for such poor performance

with the 0.5M is attributed to the high hydrogen ion concentration in the digested feed sludge. The Donnan Dialysis process works by exchanging aluminium ions in the feed for hydrogen ions in the sweep. If the feed and sweep both contain the same concentration of hydrogen ions (0.5M acid was used for the sweep), then the electrochemical potential between the two sides of the membrane becomes similar, this is turn slows down kinetics. The aluminium from the 0.05M digested sludge can still yield high recoveries because a driving force of at least an order of magnitude difference (0.05M hydrogen ion is feed and 0.5M in sweep) still exists.

4.6.6 Summary

In summary, two acids concentrations were used for digesting the sludge, namely 0.5M and 0.05 M HCl. The stronger acid was found to breakdown the sludge more efficiently. The starting concentration of aluminium in the 0.5M sludge was found to be 600 mg/L while that of the 0.05 M acid was 300 mg/L. The concentration of organics in the stronger concentration digestion was also higher than that of the weaker.

The 0.5 M acid was found to have a recovery of 42% after 20 hours and 44% after 48hours. The 0.05 M acid was found to yield a 97% recovery after 20 hours and 85% after 48 hours. The large difference was found to be due to the lack of an electrochemical potential driving force in the 0.5 M digestion as it was the same concentration of acid used to drive the reaction from the sweep side. The membrane was found to reject 97% of organics for the first 24 hours of the experiment and 94% for the next 24 hours (until 48hours). It would seem that running the investigation for 20-24 hours is sufficient, as further running time reduces the final aluminium recovery and also increases the organics transported to the sweep side.

4.7 Supplementary notes

It should be noted that in additional to a statistical model being formulated to represent the results obtained, a fundamental model was also constructed. It made use of the Nernst-Planck equations to calculate the fluxes and concentrations of aluminium in the system at any point in time. The objective was to then compare these two models in terms of representing the data accurately. The fundamental model calculated was found to not represent the experimental data and was thus omitted from the report.

Secondly, in terms of membrane fouling, most of the experimental work for the project was conducted on a synthesized feed of Alum with no contaminants present. With this said, no fouling or marked performance decline in the membrane was spotted over the two year investigation. It would however be inaccurate to say that the Nafion 117 membrane was immune to fouling as more rigorous tests with organics for prolonged periods would have to be conducted first.

Chapter 5 Conclusion and recommendations

5.1 Introduction

The aims and objectives of this study were to:

1. To identify and investigate the optimal flow rates and concentrations to maximize the recovery of aluminium ions from water treatment residuals in a laboratory scale Donnan Dialysis cell.

2. Investigate if DD can selectively recover aluminium ions, whilst rejecting organics? If so, by how much?

5.2 Scanning Investigations

The effects of feed concentration, sweep concentration, feed flow rate and sweep flow rate on the final aluminium concentration were investigated. The sweep concentration of aluminium was found to rapidly increase in the first 24 hours of experimentation and then was found to taper off and subsequently decrease in the next 24 hours. Osmotic water transport from the feed to the sweep side was found to critically influence the final aluminium sweep concentration.

The most significant variables which influenced the final aluminium concentration in the sweep side were initial feed concentration, initial sweep concentration and feed flow rate. The effect of sweep flow rate was found not to be as significant.

Varying the feed flow rate was found to increase the final aluminium ion concentration by at least 700 mg/L in favour of lower flow rates. Higher initial acid sweep concentrations were found to increase the aluminium ion concentration in the sweep by at least 1400 mg/L.

Lastly, the feed concentration was found to be a function of the initial sweep acid concentration. A higher concentration of aluminium was recovered in the sweep for high initial feed concentrations only when high initial acid sweep concentrations were used. A higher aluminium concentration was recovered in the sweep using low feed concentration when low acid sweep concentrations were used.

5.3 Modelling and optimization of the DD process for optimal recoveries

New operating conditions reflecting typical concentration ranges of aluminium in water treatment residuals were used. Sweep acid concentrations were reduced to mitigate osmotic water transport from the feed to the sweep. From the experiments performed at the new operating conditions, a statistical model was developed using natural variables to determine the relationship of the variables to the final aluminium recovery. It is as follows:

$$Y_{recovery} = 2.13 \times 10^{2} - 32.7X_1 - 1.70 \times 10^{-1}X_2 + 28.7X_3 + 3.40{X_1}^2 - 78.8{X_3}^2 +$$

$$5.00 \times 10^{-4}X_1X_2 + 2.40 \times 10^{-1}X_1X_3 + 1.00 \times 10^{-1}X_2X_3$$

Where: X_1 is the feed flow rate (mL/s)

X_2 is the initial feed concentration (mg/L)

X_3 is the initial sweep concentration (M)

Predicted data was plotted against the actual data. An R^2 value of 0.99 was found, indicating the similarity of the predicted data from the actual experimental data. Subsequently, an F test was used in order to assess the significance of the model. The model was found to be significant with an F critical value of 2.48 and F value of 1.06 being obtained.

Surface plots were generated from the statistical model. It was found that a combination of low feed concentrations, low feed flowrates and moderate acid concentrations were found to yield the highest recoveries of aluminium. The highest recoveries of aluminium in the sweep were found to be 97-98 %.

Statistical analysis of the variables in the model at a confidence interval of 95% revealed that, feed concentration was found to be the most significant parameter, the p value was found to be 0.00. Both sweep concentration and feed flow rate were found to be statistically insignificant with p values of 0.375 and 0.301 respectively.

5. 4 Real water treatment residuals

Lastly, investigations were conducted on water treatment residuals in the form of sludge. Two acids concentrations were used for digesting the sludge, namely 0.5 M and 0.05 M HCl. The stronger acid was found to breakdown the sludge more efficiently. The starting concentration of aluminium in the 0.5 M sludge was found to be 600 mg/L while that of the 0.05 M acid was 300 mg/L.

After Donnan Dialysis experimentation, a recovery of 42 % of aluminium ions after 20 hours and 44 % after 48 hours was obtained from the feed of the water treatment residuals which were digested with 0.5 M acid. The 0.05 M digested water treatment residuals feed was found to yield a 97 % recovery after 20 hours and 85 % after 48 hours.

UV 254 analysis revealed that organics from the feed to the sweep were rejected by at least 94%

5.5 Summary of technical performance of the DD module

1.) Can Donnan Dialysis selectively recover aluminium from water treatment residuals whilst rejecting organics?

Donnan Dialysis was found to selectively recover aluminium whilst rejecting organics by up to 97% in the first 24 hours of operation.

2.) What is the maximum recovery of aluminium that can be achieved?

The maximum recovery of aluminium using synthetic feed was found to be 98%. When real water treatment residuals were used, a 97% recovery of aluminium was obtained in the first 24 hours of operation.

3.) What is the maximum concentration of aluminium that can be achieved?

The new operating conditions were found to greatly reduce water transport and thus mitigate dilution of the sweep concentration. Water transport from the feed to the sweep with these new conditions was found to be about 20 mL. This therefore meant the aluminium in the feed could be concentrated up to 2.8- 2.9 times in the sweep.

4.) Can the recovered aluminium be directly reused in treatment plants?

No, the aluminium would need to further be concentrated in order to be reused. Nano filtration is a potential option.

5.6 Future recommendations

The following future recommendations are suggested:

The use of scanning electron microscopy (SEM) to analyse the surface of the Nafion 117 membrane in order to determine if there are regions of active sites and dead zones will be a useful addition in future. This process will help get a better understanding of the effect of flow patterns and deposition mechanisms.

Secondly, the use of cations of different sizes and valences in the feed along with aluminium will greatly aid in assessing the selectivity of the membrane for aluminium. This will also help in conducting a techno-economic assessment because some water treatment plants have been known to dose with more than one cation. Examples include sodium and aluminium used in unison.

Lastly, performing rigorous runs containing organic contaminants in the feed to assess the fouling characteristics of the membrane will determine if this process is feasible in the long term.

6 Bibliography

Agarwal, C., Cattrall, R. and Kolev, S. (2016). Donnan dialysis based separation of gold(III) from electronic waste solutions using an anion exchange pore-filled membrane. *Journal of Membrane Science*, 514, pp.210-216.

Akretche, D. (2000). Donnan dialysis of copper, gold and silver cyanides with various anion exchange membranes. Talanta, 51(2), pp.281-289.

Altmann, P., Cunningham, J., Dhanesha, U., Ballard, M., Thompson, J. and Marsh, F. (1999). Disturbance of cerebral function in people exposed to drinking water contaminated with aluminium sulphate: retrospective study of the Camelford water incident. BMJ, 319(7213), pp.807-811.

American Water Works Association (2003). Water treatment. 3rd ed. Denver, CO: American Water Works Association, pp.1-11.

Asano, T. (1988). Wastewater reclamation and reuse. Water Pollution Control Federation, 60(6), pp.854-856.

Asano, T., and Levine, A.D. (1995). Wastewater Reuse: A Valuable Link in Water Resources Management. Water Quality International, No. 4, pp. 20-24.

Baker, R. (2013). Membrane technology and applications. 2nd ed. Hoboken, N.J.: Wiley.

Ben Hamouda, S., Touati, K. and Ben Amor, M. (2017). Donnan dialysis as membrane process for nitrate removal from drinking water: Membrane structure effect. Arabian Journal of Chemistry, 10, pp.S287-S292.

Bhuttacharjee, S. (2017). *Concentration Polarization*. [online] Waterplanet.com. Available at: http://www.waterplanet.com/wp-content/uploads/2017/07/ConcentrationPolarization_FINAL_7-11-17.pdf [Accessed 3 Apr. 2018].

Callister, W. and Rethwisch, D. (2015). Materials Science and Engineering. 8th ed.New York: John Wiley & Sons Inc.

Cheng, W., Chen, P., Tian, D., Yu, R. and Fu, C. (2016). Use of Nanofiltration membranes to concentrate and recover leached aluminium from acidified water treatment sludge. Environment Protection Engineering, 42(3), pp.19-33.

Cheryan, M. (1998). Ultrafiltration and microfiltration. 1st ed. Boca Raton [et al.]: CRC Press.

Chusid, J., Pacella, B., Kopeloff, L. and Kopeloff, N. (1951). Chronic Epilepsy in the Monkey Following Multiple Intracerebral Injections of Alumina Cream. Experimental Biology and Medicine, 78(1), pp.53-54

Cengeloglu, Y., Kir, E., Ersoz, M., Buyukerkek, T. and Gezgin, S. (2003). Recovery and concentration of metals from red mud by Donnan dialysis. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 223(1-3), pp.95-101.

City of Cape Town (2018). Water services and the Cape Town urban water cycle. Cape Town, pp.1-40.

Cloete, K. (2017). Recyling wastewater an option to counter water scarcity. [0nline] engineeringnews.co.za. Available at: http://www.engineeringnews.co.za/article/recycling-waste-water-an-option-to-counter-water-scarcity. [Accessed 12th November 2018]

Cotruvo, J. (2017). 2017 WHO Guidelines for Drinking Water Quality: First Addendum to the Fourth Edition. Journal - American Water Works Association, 109, pp.44-51.

Davis, T. (2001). Donnan Dialysis. The Encyclopedia of Separation Science, 4(1), pp.1701-1707.

Duan, Q., Wang, H. and Benziger, J. (2011). Transport of liquid water through Nafion membranes. Journal of Membrane Science, 392-393, pp.88-94.

Eikerling, M. (1998). Phenomenological Theory of Electro-osmotic Effect and Water Management in Polymer Electrolyte Proton-Conducting Membranes. Journal of The Electrochemical Society, 145(8), p.2684.

Evuti M.A, Lawal M, 2011 'Recovery of coagulants from water works sludge: A review'. Advances in Applied Science Research,2(6),pp. 410-417

Gjelstad, A., Rasmussen, K. and Pedersen-Bjergaard, S. (2007). Simulation of flux during electro-membrane extraction based on the Nernst–Planck equation. Journal of Chromatography A, 1174(1-2), pp.104-111.

Hariembrundtland, G. (1987). World Commission on environment and development. Environmental Policy and Law, 14(1), pp.26-30.

Hart, S. (1996). Beyond greening: Strategies for a sustainable world. Harvard Buisiness Review, 75(1), pp.65-75.

Hichour, M., Persin, F., Sandeaux, J. and Gavach, C. (1999). Fluoride removal from waters by Donnan dialysis. Separation and Purification Technology, 18(1), pp.1-11.

Ho, C., Jan, D. and Tsai, F. (1993). Membrane diffusion-controlled kinetics of ionic transport. Journal of Membrane Science, 81(3), pp.287-294.

Keeley, J., Jarvis, P. and Judd, S. (2012). An economic assessment of coagulant recovery from water treatment residuals. Desalination, 287, pp.132-137.

Keeley, J., Jarvis, P. and Judd, S. (2014). Coagulant Recovery from Water Treatment Residuals: A Review of Applicable Technologies. Critical Reviews in Environmental Science and Technology, 44(24), pp.2675-2719.

Kawahara, M. and Kato-Negishi, M. (2011). Link between Aluminum and the Pathogenesis of Alzheimer's Disease: The Integration of the Aluminum and Amyloid Cascade Hypotheses. International Journal of Alzheimer's Disease, 2011, pp.1-17.

Kowalski, S. and Montgomery, D. (2013). Design and analysis of experiments. 2nd ed. Hoboken, NJ: J. Wiley & Sons.

Marzouk, I., Dammak, L., Chaabane, L. and Hamrouni, B. (2013). Optimization of Chromium (Vi) Removal by Donnan Dialysis. American Journal of Analytical Chemistry, 04(06), pp.306-313.

Mihelcic, J., Zimmerman, J. and Auer, M. (2010). Environmental engineering. 2nd ed. John Wiley & Sons.

Miyoshi, H. (1997). Diffusion coefficients of ions through ion-exchange membranes for Donnan dialysis using ions of the same valence. Chemical Engineering Science, 52(7), pp.1087-1096.

Moshtarikhah, S., Oppers, N., de Groot, M., Keurentjes, J., Schouten, J. and van der Schaaf, J. (2016). Nernst–Planck modeling of multicomponent ion transport in a Nafion membrane at high current density. Journal of Applied Electrochemistry, 47(1), pp.51-62.

Napoli, L., Franco, J., Fasoli, H. and Sanguinetti, A. (2014). Conductivity of Nafion® 117 membrane used in polymer electrolyte fuel cells. International Journal of Hydrogen Energy, 39(16), pp.8656-8660.

Napoli, L., Lavorante, M.J., Franco, J., Sanguinetti, A., and Fasoli, H, (2013) ,Effect on Nafion 117 membrane using different strong acids in various concentrations. Journal of New Materials For Electrochemical Systems ,16 (3),pp 151-156

Nwal Amang, D. (2004). Mass transfer characterization of Donnan dialysis in a bi-ionic chloride–nitrate system. Chemical Engineering Journal, 99(1), pp.69-76.

Nwal Amang, D., Alexandrova, S. and Schaetzel, P. (2003). Bi-ionic chloride-nitrate equilibrium in a commercial ion-exchange membrane. Desalination, 159(3), pp.267-271.

Okada, T., Xie, G., Gorseth, O., Kjelstrup, S., Nakamura, N. and Arimura, T. (1998). Ion and water transport characteristics of Nafion membranes as electrolytes. Electrochimica Acta, 43(24), pp.3741-3747.

Prakash, P. (2004). Application of homogeneous and heterogeneous cation-exchange membranes in coagulant recovery from water treatment plant residuals using Donnan membrane process. Journal of Membrane Science, 237(1-2), pp.131-144.

Prakash, P. and SenGupta, A. (2004). Modeling Al3+/H+ ion transport in Donnan membrane process for coagulant recovery. *AIChE Journal*, 51(1), pp.333-344.

Prakash, P. and SenGupta, A. (2003). Selective Coagulant Recovery from Water Treatment Plant Residuals Using Donnan Membrane Process. *Environmental Science & Technology*, 37(19), pp.4468-4474.

Poźniak, G. and Trochimczuk, W. (1990). Tubular interpolymer ion-exchange membranes. Donnan dialysis through strong-base membranes. *Journal of Membrane Science*, 49(1), pp.55-68.

Rand Water. (2018).The water situation. [0nline] www.waterwise.co.za. Available at: http://www.waterwsie.co.za/export/sites/water/waterwise_water_situation_in_South_Africa. [Accessed 12th November 2018]

Rhodes, M. (2013). Introduction to Particle Technology. 2nd ed. New York, NY: John Wiley & Sons.

Rice, J. (1995). Mathematical statistics and data analysis. 3rd ed. California: Duxbury press.

Sarkar, S., SenGupta, A. and Prakash, P. (2010). The Donnan Membrane Principle: Opportunities for Sustainable Engineered Processes and Materials. Environmental Science & Technology, 44(4), pp.1161-1166

Sionkowski, G. and Wódzki, R. (1995). Recovery and Concentration of Metal Ions. I. Donnan Dialysis. *Separation Science and Technology*, 30(5), pp.805-820.

Smith, J., Van Ness, H., Abbott, M. and Swihart, M. (2001). Introduction to chemical engineering thermodynamics. 8th ed. New York: McGraw Hill education.

Spofforth, J. (1921). Case of aluminium poisoning. The Lancet, 197(5103), p.1301.

Tredoux, F. (2016). Steenbras WTP chemical return report. Sommerset West: City of Cape Town, pp.1-25.

Tripathy,S.K and Rama Murthy,Y. (2012). Modelling and optimization of spiral concentrator for separation of ultrafine chromite. Journal of Powder Technology,221,pp.387-394

Tor, A., Çengeloğlu, Y., Ersöv, M. and Arslan, G. (2004). Transport of chromium through cation-exchange membranesby Donnan dialysis in the presence of some metals of different valences. *Desalination*, 170(2), pp.151-159.

van Rooyen, M. (2012). *Aluminium recovery using Donnan Dialysis*. Undergraduate. Stellenbosch University.

Wallace, R. (1967). Concentration and Separation of Ions by Donnan Membrane Equilibrium. *Industrial & Engineering Chemistry Process Design and Development*, 6(4), pp.423-431.

Wang, Q., Lenhart, J. and Walker, H. (2010). Recovery of metal cations from lime softening sludge using Donnan dialysis. Journal of Membrane Science, 360(1-2), pp.469-475.

Wiśniewski, J. and Różańska, A. (2006). Donnan dialysis with anion-exchange membranes as a pretreatment step before electrodialytic desalination. *Desalination*, 191(1-3), pp.210-218.

XiaoJin Li, ChangChun Ke, ShuGuo Qu, Jin Li, ZhiGang Shao and BaoLian Yi (September 22nd 2011). High Temperature PEM Fuel Cells Based on Nafion®/SiO2 Composite Membrane, Energy Storage in the Emerging Era of Smart Grids Rosario Carbone, IntechOpen, DOI: 10.5772/19029. Available from: https://www.intechopen.com/books/energy-storage-in-the-emerging-era-of-smart-grids/high-temperature-pem-fuel-cells-based-on-nafion-sio2-composite-membrane

Xu, G., Yan, Z., Wang, Y. and Wang, N. (2009). Recycle of Alum recovered from water treatment sludge in chemically enhanced primary treatment. Journal of Hazardous Materials, 161(2-3), pp.663-669.

XU, T. (2005). Ion exchange membranes: State of their development and perspective. Journal of Membrane Science, 263(1-2), pp.1-29.

Xue, T., Longwell, R. and Osseo-Asare, K. (1991). Mass transfer in Nation membrane systems: Effects of ionic size and charge on selectivity. Journal of Membrane Science, 58(2), pp.175-189.

Zhao, B., Zhao, H. and Ni, J. (2010). Arsenate removal by Donnan dialysis: Effects of the accompanying components. *Separation and Purification Technology*, 72(3), pp.250-255.

Appendix A: Raw data

Appendix A provides the raw data from the experiments performed in the DD investigation.

Table A-1 provides the data for the calibration of the peristaltic pumps used.

Table A-1: Pump calibrations

Time (s)	Setting (%)	Volume(mL)	Flow rate(mL/s)	Average
215	25	400	1.86	
173	25	400	2.31	
174	25	400	2.29	2.16
132	50	400	3.03	
120	50	400	3.33	
115	50	400	3.48	3.29
91	75	400	4.40	
90	75	400	4.44	
84	75	400	4.76	4.53
72	100	400	5.56	
67	100	400	5.97	
66	100	400	6.06	5.86

Table A-2 provides the data points for the mass balance and verification investigation conducted in section 4.2.2 of the thesis.

Table A-2: Mass balance and verification investigation

Time(hrs)	Feed (mg/L)	Sweep(mg/L)
0	3100	0
2	3052	1595
4	2784	3318
20	874	6337
22	785	6949
24	756	7503
44	401	7980
46	400	7621
48	400	7620

Table A-3 tabulates the data obtained from the AAS investigation to determine the repeatability and accuracy of the experiment done over three days. The Cal-Std are the calibration standards used. QC is the quality control standard. Lastly the LP# is the sample number tested. The Figures produced from this data and results are provided in Appendix D.

Table A-3: AAS investigation data

	Std/sample		**Units**	**Conc**
Day 1				
36	Cal-Std1	Al309	mg/L	2.00
37	Cal-Std2	Al309	mg/L	10.00
38	Cal-Std3	Al309	mg/L	20.00
39	Cal-Std4	Al309	mg/L	50.00
40	Cal-Std5	Al309	mg/L	100.00
43	**QC JFG**	**Al309**	**mg/L**	**21.51**
44	LP Al #1	Al309	mg/L	4.80
45	LP Al #2	Al309	mg/L	25.67
46	LP Al #3	Al309	mg/L	56.48
47	LP Al #4	Al309	mg/L	4.70

48	LP Al #5	Al309	mg/L	25.49
49	LP Al #6	Al309	mg/L	52.40
50	**QC JFG**	**Al309**	**mg/L**	**21.41**
Day2				
52	Cal-Std1	Al309	mg/L	2.00
53	Cal-Std2	Al309	mg/L	10.00
54	Cal-Std3	Al309	mg/L	20.00
55	Cal-Std4	Al309	mg/L	50.00
56	Cal-Std5	Al309	mg/L	100.00
59	**QC JFG**	**Al309**	**mg/L**	**21.04**
60	LP Al #1	Al309	mg/L	4.70
61	LP Al #2	Al309	mg/L	24.70
62	LP Al #3	Al309	mg/L	52.74
63	LP Al #4	Al309	mg/L	4.58
64	LP Al #5	Al309	mg/L	24.48
65	LP Al #6	Al309	mg/L	50.38
66	**QC JFG**	**Al309**	**mg/L**	**20.72**
67	LP Al #1	Al309	mg/L	4.76
68	LP Al #2	Al309	mg/L	4.85
69	LP Al #3	Al309	mg/L	24.23
70	LP Al #4	Al309	mg/L	24.13
71	LP Al #5	Al309	mg/L	49.71
72	LP Al #6	Al309	mg/L	49.41
73	**QC JFG**	**Al309**	**mg/L**	**20.46**
Day3				
75	Cal-Std1	Al309	mg/L	2.00
76	Cal-Std2	Al309	mg/L	10.00
77	Cal-Std3	Al309	mg/L	20.00

78	Cal-Std4	Al309	mg/L	50.00
79	Cal-Std5	Al309	mg/L	100.00
82	**QC JFG**	**Al309**	**mg/L**	**21.12**
83	LP Al #1	Al309	mg/L	4.47
84	LP Al #2	Al309	mg/L	24.88
85	LP Al #3	Al309	mg/L	52.53
86	LP Al #4	Al309	mg/L	4.24
87	LP Al #5	Al309	mg/L	23.76
88	LP Al #6	Al309	mg/L	50.60
89	**QC JFG**	**Al309**	**mg/L**	**20.83**
90	LP Al #1	Al309	mg/L	4.02
91	LP Al #2	Al309	mg/L	4.39
92	LP Al #3	Al309	mg/L	24.89
93	LP Al #4	Al309	mg/L	23.72
94	LP Al #5	Al309	mg/L	50.94
95	LP Al #6	Al309	mg/L	49.30
96	**QC JFG**	**Al309**	**mg/L**	**20.18**
97	LP AL #1	Al309	mg/L	50.70
98	LP AL #2	Al309	mg/L	50.29
99	LP AL #3	Al309	mg/L	24.52
100	LP AL #4	Al309	mg/L	24.31
101	LP AL #5	Al309	mg/L	4.43
102	LP AL #6	Al309	mg/L	4.58
103	**QC JFG**	**Al309**	**mg/L**	**20.63**

Tables A-4 provides the aluminium feed and sweep concentrations for the 0.5M and 0.05M acid digestions of the WTRs. Table A-5 tabulates the data obtained from the UV analysis for organics in both the feed and sweep of the WTR samples.

Table A-4: Aluminium feed and sweep concentrations

Time(hrs)	Feed@ 0.5M acid digestion	Sweep @ 0.5M acid digestion	Feed@ 0.05M acid digestion	Sweep@ 0.05M acid digestion
0	600	0	310	0
2	586.3	82.2	153.5	579.9
18	502.9	132.7	119	770.3
20	464.2	256	3.53	900
23	374.9	253.3	4	636.5
41	411.4	249.8	4.3	639.1
46	321.1	248.9	7.6	739
48	294.9	263.9	7.6	779.2

Table A-5: UV-vis analysis of WTRs

Time (hrs)	Feed at 0.05M acid digestion	Sweep at 0.05M acid digestion	Feed at 0.5M acid digestion	Sweep at 0.5M acid digestion
0	19.18	12.08	20.57	12.09
2	17.78	12.67	20.89	12.3
18	18.39	12.69	20.46	12.4
20	18.4	12.64	20.27	12.48
23	18.03	12.3	20.15	12.2
41	17.97	13.02	19.87	12.61
46	17.87	13.41	19.31	13.06

Table A-6 below displays the data for the full factorial design conducted and Table A-7 displays the Box Behnken data.

Table A-6: Full factorial design data

3000mg/L feed, 2M Sweep, 2.2 mL/s feed flow,2.2 mL/s sweep flow			
	mg/L	mg/L	
Time(hrs)	Feed side	Sweep side	
0	3000	0	
3	2638	1155	
5	2657	1955	
22	968.3	5670	
25	801.5	6920	
28	801	5221	
46	545.6	6335	
2000mg/L feed, 1M sweep, 4.9 mL/s feed flow, 4.9 mL/sweep flow			
	mg/L	mg/L	
Time(hrs)	Feed side	Sweep side	
0	2000	0	
3	1934	642	
5	1686	1015	
22	998.5	2880	
25	973.1	3115	
28	848.8	2913	
46	589.1	3248	
3000mg/L feed, 1M sweep, 2.2 mL/s feed flow, 2.2 mL/s sweep flow			

	mg/L	mg/L	
Time(hrs)	Feed side	Sweep side	
0	3300	0	
3	3230	1008	
5	3022	1552	
22	1852	3717	
25	1798	3817	
28	1872	5918	
46	1729	4950	
3000mg/L feed, 1M sweep, 4.9 mL/s feed flow, 4.9 mL/s sweep flow			
	mg/L	mg/L	
Time(hrs)	Feed side	Sweep side	
0	3000	0	
3	2465	1146	
5	1561	1750	
22	1440	3859	
25	1644	3635	
28	1444	4109	
46	1523	3871	
2000mg/L feed, 2M sweep, 2.2 mL/s feed flow, 2.2 mL/s sweep flow			
	mg/L	mg/L	
Time(hrs)	Feed side	Sweep side	
0	2100	0	
3	2082	977	
5	557	1457	

22	407.3	3785	
25	349.7	4313	
28	111.2	3608	
46	139.5	2581	
3000mg/L feed, 2M sweep, 4.9 mL/s feed flow, 4.9 mL/s sweep flow			
	mg/L	mg/L	
Time(hrs)	Feed side	Sweep side	
0	3100	0	
2	3052	1595	
4	2784	3318	
20	874	6337	
22	785	6949	
24	756	7503	
44	401	7980	
46	399	7621	
2000mg/L feed, 1M sweep, 2.2 mL/s feed flow, 2.2 mL/s sweep flow			
Time (hrs)	Feed side	Volume (mL)of water transported	Sweep side
0	2000	0	0
2	1811	0	1185
4	1765	0	1391
6	1612	0	1567
24	807.3	143	3143
26	866.1	191	3203

27.5	954.7	214	3302
29.5	977.7	231	3386
31	700.8	231	3089
47	713.2	309	3848
49	643.3	310	3772
3000mg/L feed, 2 M sweep, 4.9 mL/s feed flow, 2.2 mL/s sweep flow			
Feed side	Sweep side	Time (hrs)	Volume (mL) of water transported
3700	0	0	0
3614	2083	2	0
2919	1637	3.5	0
2668	2028	4.5	0
1280	6018	22.5	260
1129	5313	24.5	285.7
969.4	5461	27.5	333.3
1146	6175	29	333.3
456	6021	46.5	428.6
1154	6673	48	428.6
2000 mg/L feed, 1M sweep, 4.9 mL/s feed flow, 2.2 mL/s sweep			
Sweep side	Time (hrs)	Feed side	Volume (mL) of water transported
0	0	2000	0
978.1	2	1674	0
1307	4	1515	0

1783	6	1421	0
4083	24	655.8	143
3925	26	618.6	191
3789	27.5	550.3	214
3697	29.5	573.6	231
3694	31	512.5	231
3667	47	428.9	309
2000 mg/L feed, 1 M sweep, 2.2 mL/s feed flow, 4.9 mL/s sweep flow			
Feed side	Sweep side	Time(hrs)	Volume (mL) of water transported
2400	0	0	0
2337	541.2	2	0
1550	1253	3.5	0
1575	1774	4.5	0
737.4	3605	22.5	215
625.7	3478	24.5	215
600.2	3987	27.5	215
509.9	4080	29	215
1173	3862	46.5	270
1329	4463	48	285.7
3000 mg/L feed, 1M sweep, 4.9 mL/s feed flow, 2.2 mL/s sweep flow			

Sweep side	Time(hrs)	Feed side	Volume (mL of water transported
0	0	3000	0
1652	2	2831	0
1212	3	2973	0
3700	21	1789	170
4173	23	1638	203
4086	24.5	1625	220
4063	26.5	1873	240
3957	28	1591	262
4712	45	1461	310
4280	47	1222	310
2000mg/L feed, 2M sweep, 4.9 mL/s feed flow, 2.2 mL/s sweep flow			
Sweep side	Time(hrs)	Feed side	Volume (mL) of water transported
0	0	2000	0
1217	2	1788	0
1634	3	1659	0
4990	21	276	380
5465	23	150	405
4551	24.5	91.8	425
4718	26.5	70.2	450
4730	28	57.6	480
4713	45	40.59	670

4710	47	41.65	670

Table A-7: Box Behnken design data

1		300mg/L feed, 0.5 M sweep, 3.5 mL/s feed flow		
	Time (hrs)	Feed side	Sweep side	Recovery (%)
	0	300	0	0.0
	18	3.7	945	105.0
	21	1.7	897	99.7
	43	0.65	899	99.9
	45	0.18	899	99.9
	48	0.47	895	99.4
2		300mg/L feed, 0.5 M sweep,5.5 mL/s feed flow		
	Time (hrs)	Feed side	Sweep side	Recovery (%)
	0	300	0	0.0
	18	0	899	99.9
	21	0.8	901	100.1

	43	0	869	96.6
	45	0	877	97.4
	48	0	877	97.4
3		500mg/L feed, 0.5M sweep,4.5 mL/s feed flow		
	Time (hrs)	Feed side	Sweep side	Recovery (%)
	0	500	0	0.0
	2	270	710	47.3
	4	21.8	1060	70.7
	27	14.3	1048	69.9
	46	17.3	1048	69.9
	48	17.8	1112	74.1
		700mg/L feed,0.5 M sweep,3.5 mL/s feed flow		
4				
	Time (hrs)	Feed side	Sweep side	Recovery(%)
	0	700	0	0.0
	2.5	500	623	29.7
	4.5	361	900	42.9
	21.5	60.5	1158	55.1

	26	43.2	1195	56.9
	27	49.4	1200	57.1
	46	67.6	1244	59.2
	48	63.6	1214	57.8
5		700mg/L feed,0.5 M sweep, 5.5 mL/s feed flow		
	Time(hrs)	Feed side	Sweep side	Recovery (%)
	0	700	0	0.0
	2.5	484	548.8	26.1
	4.5	346	822	39.1
	21.5	42.3	1221	58.1
	26	28.6	1180	56.2
	27	34.9	1164	55.4
	46	52.3	1200	57.1
	48	56.5	1180	56.2
6		500 mg/L feed,0.25M sweep, 3.5 mL/s feed flow		
	Time(hrs)	Feed side	Sweep side	Recovery (%)
	0	500	0	0.0

	2	356	625	41.7
	3.5	342	794	52.9
	5	312	835	55.7
	23	134	1105	73.7
	25	103	1142	76.1
	27	77.4	1100	73.3
	44	124	1095	73.0
	46	120	1085	72.3
7		500 mg/L feed, 0.25M sweep, 5.5 mL/s feed flow		
	Time (hrs)	Feed side	Sweep side	Recovery (%)
	0	500	0	0.0
	2	380.7	512.5	34.2
	3.5	306.1	626.2	41.7
	5	307.7	731.6	48.8
	23	108.5	1061	70.7
	25	95.2	1049	69.9
	27	84.84	1034	68.9
	44	97.08	1017	67.8
	46	95	1016	67.7
8		500mg/L feed, 0.5M sweep, 4.5 mL/s feed flow		

	Time (hrs)	Feed side	Sweep side	Recovery (%)
	0	500	0	0.0
	2	344.4	527	35.1
	3.5	8.85	1066	71.1
	22	5.393	1080	72.0
	24	4.488	995	66.3
	27	8.12	1066	71.1
	46	8.87	1138	75.9
	48	10.47	1097	73.1
9		500 mg/L feed, 0.75M sweep, 3.5 mL/s feed flow		
	Time (hrs)	Feed side	Sweep side	Recovery (%)
	0	500	0	0.0
	2	244	740	49.3
	20	4.1	1290	86.0
	35	0.4	1088	72.5
	42	0.77	1225	81.7
	48	0.44	1162	77.5

10				
		500 mg/L feed, 0.75M sweep, 5.5 mL/s feed flow		
	Time (hrs)	Feed side	Sweep side	Recovery (%)
	0	500	0	0.0
	3.5	273	773.1	51.5
	21	6.5	1082	72.1
	23	4.5	1086	72.4
	25	1.1	1011	67.4
	44	1.6	915	61.0
	46	2.1	1046	69.7
	48	2.3	1092	72.8
11		300mg/L feed, 0.25M sweep, 4.5 mL/s feed flow		
	Time (hrs)	Feed side	Sweep side	Recovery (%)
	0.0	300.0	0.0	0.0
	1.5	223.0	327.2	36.4
	3.0	140.0	526.7	58.5

	22.0	12.9	822.7	91.4
	26.0	11.2	832.4	92.5
	28.0	10.5	840.3	93.4
	46.5	13.6	762.6	84.7
	48.0	14.1	856.6	95.2
		700 mg/L feed, 0.25M, 4.5 mL/s feed flow		
12.0				
	Time (hrs)	Feed side	Sweep side	Recovery (%)
	0.0	700.0	0.0	0.0
	1.5	617.9	228.5	10.9
	3.0	490.0	566.7	27.0
	22.0	250.4	936.0	44.6
	26.0	237.1	970.1	46.2
	28.0	261.6	941.4	44.8
	46.5	259.5	913.1	43.5
	48.0	259.0	962.6	45.8
		300 mg/L feed, 0.75M, 4.5 mL/s feed flow		
13				

	Time (hrs)	Feed side	Sweep side	Recovery (%)
	0.0	300.0	0.0	0.0
	2.5	173.0	426.6	47.4
	5.0	56.6	625.6	69.5
	23.5	0.0	763.5	84.8
	24.5	0.0	755.1	83.9
	27.5	0.0	748.4	83.2
	29.5	0.0	750.2	83.4
	48.0	0.0	769.5	85.5
14				
		700 mg/L feed, 0.75M sweep, 4.5 mL/s feed flow		
	Time (hrs)	Feed side	Sweep side	Recovery (%)
	0.0	700.0	0.0	0.0
	2.5	506.0	687.0	32.7
	5.0	301.0	957.0	45.6
	23.5	11.2	1140.0	54.3
	24.5	9.5	1190.0	56.7
	27.5	8.9	1196.0	57.0
	29.5	8.2	1146.0	54.6
	48.0	16.0	1142.0	54.4

15		500mg/L feed,0.5M sweep, 4.5 mL/s		
	time	Feed side	Sweep side	Recovery (%)
	0	500.0	0.0	0.0
	2	278.0	472.0	31.5
	4	9.1	1099.0	73.3
	22	8.3	1076.0	71.7
	24	8.3	1084.0	72.3
	27	13.7	1067.0	71.1
	46	14.7	1025.0	68.3
	48	15.2	1088.0	72.5

The Matlab code provided below was used to generate the surface plots for the optimization in section 4.5.

```
%constant feed concentration
[A,B] = meshgrid(3.5:0.1:5.5,0.25:0.1:0.75)
X2=300
Y=212.98-32.65*A-0.17*(X2)+28.70*B+(3.4*(A).^2)-78.78*((B).^2)+
0.0005*A*X2+0.24*A.*B+0.1*X2*B
surf(A,B,Y)
ylabel('Feed flow rate (ml/s)')
xlabel('Sweep concentration(M)')
zlabel('Aluminium recovery(%)')

%constant feed flow
[A,B] = meshgrid(300:10:700,0.25:0.1:0.75)
X2=3.5
Y=212.98-32.65*X2-0.17*A+28.7*B+(3.4*(X2)^2)-
78.78*((B).^2)+0.0005*X2*A+0.24*X2*B+0.1*A.*B
%C=A.*B
surf(A,B,Y,C)
%colorbar
```

```
ylabel('Feed concentration (mg/l)')
xlabel('Sweep concentration(M)')
zlabel('Aluminium recovery(%)')

%constant sweep concentration

[A,B] = meshgrid(300:10:700,3.5:0.1:5.5)
X2=0.25
Y=212.98-32.65*B-0.17*(A)+28.70*X2+(3.4*(B).^2)-78.78*((X2)^2)+
0.0005*A.*B+0.24*B.*X2+0.1*X2*A
surf(A,B,Y)
ylabel('Feed flow rate (ml/s)')
xlabel('Feed concentration(mg/l)')
zlabel('Aluminium recovery(%)'m)
```

Tables A-8 to A-11 below provide the data and calculations used for modelling in section 4.5.3.

Table A-8: Statistical modelling data

X=

		X_1	X_2	X_3	X_{12}	X_{22}	X_{33}	$X_1 X_2$	$X_1 X_3$	$X_3 X_2$
		flow rate (ml/s)	Feed Conc	Sweep Conc						
			mg/L)	(mg/L)						
1	1	3.5	300	0.5	12.25	90000	0.25	1050	1.75	150
2	1	5.5	300	0.5	30.25	90000	0.25	1650	2.8	150
3	1	4.5	500	0.5	20.25	250000	0.25	2250	2.3	250
4	1	3.5	700	0.5	12.25	490000	0.25	2450	1.8	350
5	1	5.5	700	0.5	30.25	490000	0.25	3850	2.8	350
6	1	3.5	500	0.25	12.25	250000	0.06	1750	0.9	125
7	1	5.5	500	0.25	30.25	250000	0.06	2750	1.4	125
8	1	4.5	500	0.5	20.25	250000	0.25	2250	2.3	250
9	1	3.5	500	0.7	12.25	250000	0.49	1750	2.45	350
10	1	5.5	500	0.7	30.25	250000	0.49	2750	3.85	350
11	1	4.5	300	0.25	20.25	90000	0.06	1350	1.125	75
12	1	4.5	700	0.25	20.25	490000	0.06	3150	1.125	175
13	1	4.5	300	0.7	20.25	90000	0.49	1350	3.15	210
14	1	4.5	700	0.7	20.25	490000	0.49	3150	3.15	490
15	1	4.5	500	0.5	20.25	250000	0.25	2250	2.25	250

Table A-9: Statistical modelling data continued

X=

1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
3.5	5.5	4.5	3.5	5.5	3.5	5.5	4.5	3.5	5.5	4.5	4.5	4.5	4.5	4.5
300.0	300.0	500.0	700.0	700.0	500.0	500.0	500.0	500.0	500.0	300.0	700.0	300.0	700.0	500.0
0.5	0.5	0.5	0.5	0.5	0.3	0.3	0.5	0.7	0.7	0.3	0.3	0.7	0.7	0.5
12.3	30.3	20.3	12.3	30.3	12.3	30.3	20.3	12.3	30.3	20.3	20.3	20.3	20.3	20.3
90000.0	90000.0	250000.0	490000.0	490000.0	250000.0	250000.0	250000.0	250000.0	250000.0	90000.0	490000.0	90000.0	490000.0	250000.0
0.3	0.3	0.3	0.3	0.3	0.1	0.1	0.3	0.5	0.5	0.1	0.1	0.5	0.5	0.3
1050.0	1650.0	2250.0	2450.0	3850.0	1750.0	2750.0	2250.0	1750.0	2750.0	1350.0	3150.0	1350.0	3150.0	2250.0
1.8	2.8	2.3	1.8	2.8	0.9	1.4	2.3	2.5	3.9	1.1	1.1	3.2	3.2	2.3
150.0	150.0	250.0	350.0	350.0	125.0	125.0	250.0	350.0	350.0	75.0	175.0	210.0	490.0	250.0
6.1	15.1	10.1	6.1	15.1	3.1	7.6	10.1	8.6	21.2	5.1	5.1	14.2	14.2	10.1

Table A-10: Statistical modelling data

X^TX=

15.0	67.5	7500.0	7.3	311.8	4070000.0	4.0	33750.0	32.9	3650.0
67.5	311.8	33750.0	32.9	1474.9	18315000.0	17.8	155875.0	151.7	16425.0
7500.0	33750.0	4070000.0	3650.0	155875.0	2355000000.0	1980.0	18315000.0	16425.0	1981000.0
7.3	32.9	3650.0	4.0	151.8	1981000.0	2.3	16425.0	17.8	1980.0
311.8	1474.9	155875.0	151.7	7130.9	84577500.0	82.3	737437.5	717.9	75862.5
4070000.0	18315000.0	2355000000.0	1981000.0	84577500.0	1430300000000.0	1074200.0	10597500000.0	8914500.0	1146500000.0
4.0	17.8	1980.0	2.3	82.3	1074200.0	1.4	8910.0	10.4	1154.8
33750.0	155875.0	18315000.0	16425.0	737437.5	10597500000.0	8910.0	84577500.0	75862.5	8914500.0
32.9	151.7	16425.0	17.8	717.9	8914500.0	10.4	75862.5	82.3	8910.0
3650.0	16425.0	1981000.0	1980.0	75862.5	1146500000.0	1154.8	8914500.0	8910.0	1074200.0

Table A-11: Statistical modelling data

$(X^TX)^{-1}$ =

193.60	-62.72	-0.13	-94.39	5.54	0.00	31.60	0.01	10.77	0.03
-62.72	24.79	0.02	14.33	-2.44	0.00	-3.75	0.00	-2.39	0.00
-0.13	0.02	0.00	0.04	0.00	0.00	-0.01	0.00	0.00	0.00
-94.39	14.33	0.04	228.51	-0.40	0.00	-102.27	0.00	-22.09	-0.06
5.54	-2.44	0.00	-0.40	0.27	0.00	0.42	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
31.60	-3.75	-0.01	-102.27	0.42	0.00	108.95	0.00	0.00	0.00
0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10.77	-2.39	0.00	-22.09	0.00	0.00	0.00	0.00	4.91	0.00
0.03	0.00	0.00	-0.06	0.00	0.00	0.00	0.00	0.00	0.00

Table A-12: Statistical modelling data

$(X^TX)^{-1}X^T$ =

6.23	-0.25	-4.83	0.13	4.90	5.65	-0.59	-4.83	0.37	3.82	0.76	##########	-2.36	-0.44	-4.83
-1.85	-0.40	1.50	-0.60	-1.65	-1.82	-0.43	1.50	-0.74	-1.51	1.13	1.13	1.13	1.13	1.50
-0.01	0.00	0.00	0.00	-0.01	0.00	0.00	0.00	0.00	0.00	-0.01	0.00	0.00	-0.01	0.00
2.80	2.25	3.17	2.50	1.95	-7.91	2.58	3.17	2.61	-6.78	-5.58	0.25	0.52	-4.69	3.17
0.13	0.13	-0.17	0.13	0.13	0.13	0.13	-0.17	0.13	0.13	-0.13	##########	-0.13	-0.13	-0.17
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
-2.50	-2.50	-3.33	-2.50	-2.50	2.22	2.22	-3.33	2.78	2.78	2.22	2.22	2.78	2.78	-3.33
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
-0.06	0.06	0.00	-0.06	0.06	1.17	-1.17	0.00	-1.04	1.04	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	##########	-0.01	0.01	0.00

Table A-13: Statistical modelling data

$Y^*(X^TX)^{-1}X^T$ =

b0	212.98
b1	-32.65
b2	-0.18
b3	28.70
b4	3.41
b5	0.00
b6	-78.78
b7	0.00
b8	0.24
b9	0.10

Appendix B: Materials of construction and set up

This appendix deals with the materials of construction used for the DD experimental rig, as well as step by step instructions of the assembly of the rig.

Table B-1 below provides a list of equipment and materials necessary to construct the Donnan dialysis laboratory scale rig. It also provides a brief description of the use of that particular material or piece of equipment.

Table B-1: Materials of Construction

Quantity	**Material/Equipment**	**Use**
14	Stainless steel bolts	Fastening PVC blocks together
14	Stainless steel nuts	Fastening PVC blocks together
525 square centimeters	Silicon rubber	Sealing membrane and PVC blocks together
4*(1cm outer diameter)	PVC nozzles	To connect tubing to PVC blocks
4*(1cm outer diameter)	PVC adapters	To connect tubing to pumps
2	Positive displacement pumps	To transport feed and sweep chemicals
2*(525 Square centimeters)	PVC blocks	To house the membrane in
1*(30cm*10cm)	Membrane	Ion exchange to occur
7m length *1cm inner diameter	PTFE tubing	Transportation of fluids
8	Hose clips	To keep tubing in place at nozzles and adapters
2*5L	Glass vessels	To house feed and sweep fluids
2	Magnetic stirrers	For agitation of the solutions

Below are step by step instructions of how to assemble the rig from the equipment and materials of construction tabulated in the previous section.

The first step is to ensure that both halves of the PVC blocks have been extruded properly to accommodate both the nozzles and bolt holes required. Pictures from the top and the side of the PVC block are provided in Figure B-1 and B-2.

Figure B-1: Front view of membrane cell

Figure B-2: Side view of membrane cell

Next the nozzles are wrapped in Teflon tape to ensure no leakages between then blocks and nozzles occur. An illustration of the wrapped nozzle is provided in Figure B-3.

Figure B-3: Nozzles connecting teflon pipes to DD cell

The nozzles are then screwed into the PVC blocks. The PVC blocks are opened and the membrane is placed between them. Silicon rubber is cut out and placed around the membrane to ensure that when the PVC blocks are screwed tight there are no leaks. This is displayed in Figure B-4.

Figure B-4: Rubber and membrane placing on PVC cell

The second block is then placed on to the lower block and the blocks are tightly fastened with nuts and bolts. Four Teflon tubes are then subsequently attached to the nozzles and held in place with hose clamps as can be seen in Figure B-5.

Figure B-5: completed DD cell

Connectors which can be seen below are the screwed on to both the feed and sweep pumps. These attachments make it easier to connect the tubing to the pumps without leakages.

Figure B-6: Pump and pipe connectors

Teflon tubing is then attached to the other end of the connectors, then two 5L glass vessels are placed on mixers for continuous agitation of both feed and sweep solutions.

Figure B-7: Mixing vessel and magnetic stirrer

Lastly, the pipes are then inserted into the glass vessels, one from the pump and the other from the PVC block on both the feed and sweep side

Figure B-8: Completed DD cell setup

Appendix C: Sample calculations

Appendix C provides sample calculations for the error analysis provided in section 4.2 of the thesis. The data collected for the feed side of the runs for repeatability is displayed in C-1.

Table C-1: Data for repeat runs

Time (hrs)	0	2	4	22	24	27	46	48
Original run feed (mg/L)	500	270	21.8	10.9	8.7	14.3	17.3	17.8
Repeat1 feed (mg/L)	500	344.4	8.85	5.4	4.5	8.12	8.87	10.47
Repeat 2 feed (mg/L)	500	278.00	9.15	8.40	8.30	13.66	14.65	15.17

The mean and standard deviation for each time interval are calculated from the data in Table C-1.

E.g.: For time 2hrs, the $mean = \frac{270+344.4+278}{3} = 297.5 mg/L$

For time 0hrs the $Std\ Dev = \frac{\sqrt{((270-297.5)^2+(344.4-297.5)^2+(278-297.5))^2}}{3} = 33.34 mg/L$

Table C-2 provides the means and standard deviation of each time interval

Table C-2: Mean and standard deviation for repeat runs

Mean (mg/L)	500	297.47	13.27	8.23	7.17	12.03	13.61	14.48
Std dev	0	33.3472	6.035448	2.248456	1.892676	2.774759	3.519719	3.031974

Once the mean and standard deviation have been calculated, the value of each run in each time interval is subtracted from the mean:

$$Original\ run\ (value - mean)@\ time2hrs = 270 mg/L - 297.47 mg/L = 27.47 mg/L$$

The same is done for Repeat1 and Repeat2 at the 2hrs time interval. This yields 46.93mg/L and 19.47mg/l respectively.

The average of the values at each time interval is then calculated as follows$Average@2hrs = \frac{27.47+46.93+19.47}{3} = 31.29\ mg/$L

Lastly, the above calculated average is the divided by the mean to yield the average deviation % as follows: A$verage\ deviation\ \%@2hrs = \frac{31.29*100}{297.47} = 10.52\%$

The results are displayed in Table C-3

Table C-3: Averages and average deviations for repeat runs

Original run(value-mean)	0.00	27.47	8.53	2.67	1.53	2.27	3.69	3.32
Repeat 1(Value-mean)	0.00	46.93	4.42	2.83	2.67	3.91	4.74	4.01
Repeat 2 (value mean)	0.00	19.47	4.12	0.17	1.13	1.63	1.04	0.69
Average	0.00	31.29	5.69	1.89	1.78	2.60	3.16	2.67
Average deviation (%)	0.00	10.52	42.88	22.94	24.81	21.66	23.21	18.46

The Average % deviation in each time interval is then multiplied by the mean of each time interval for each run to provide the lower and upper boundary errors. The final concentration error bars for each time interval are displayed in Table C-4.

Table C-4: Average deviations for upper and lower limits of error bars

Time (hrs)	Mean (mg/L)	Average deviation (mg/L)	% deviation
0	500	0	0.0
2	297	±31.3	10.5
4	13	±5.7	42.9
22	8.2	±1.9	22.9
24	7.1	±1.8	24.8
27	12	±2.6	21.7
46	13	±3.2	23.2
48	14.5	±2.7	18.5

Appendix D: AAS investigation

Appendix D investigates the experiments conducted to determine the accuracy and repeatability of the AAS technique, as well as the protocol used to improve the accuracy and repeatability of using the machine.

Three different concentrations at low, medium and high levels were made up and tested, namely 500mg/L, 2500mg/L and 5000mg/L. The concentration were measured three times a day each, on three different days. Two operators were also used and their results were compared. The error bars in the below graphs show the lowest and highest reading obtained that day, and the bars are the average concentration of the day. The results are displayed in the graphs D-1 to D-3.below.

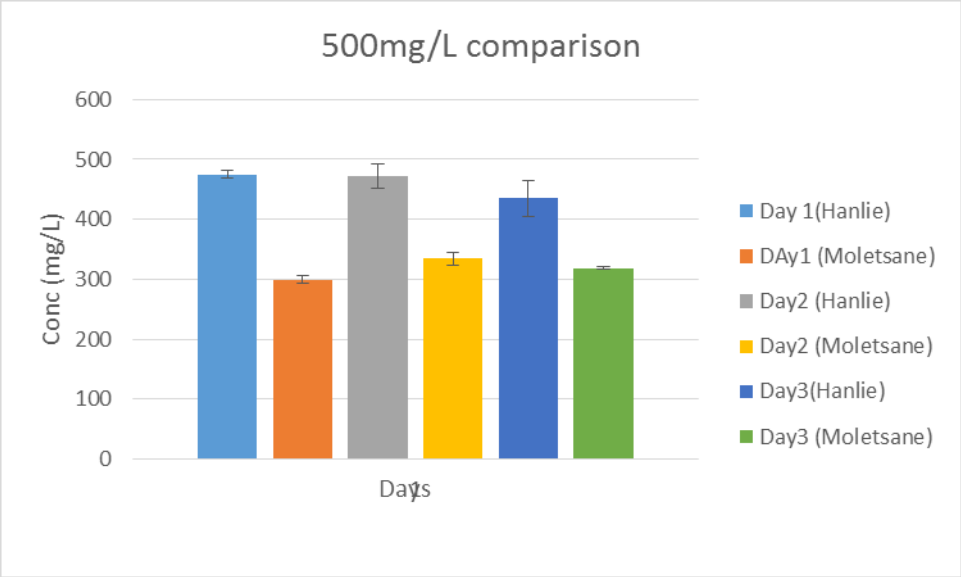


Figure D-1: AAS investigation (500 mg/L)

From Figure D-1, the three days in which operator 1 (Hanlie) measured the sample concentrations seem to yield the same average concentration in the range of 450-480mg/L of Al. The average concentration of the last day (day 3) seems to be slightly lower than the other two days, however it must also be noted that this measurement also has a higher error range associated with it. The range of measurements for operator 2 (Moletsane) on all three days were lower than that of operator 1.They ranged between 300-330mg/L. The readings of operator 2 using the same samples as operator 1 were found to be very precise but not as accurate.

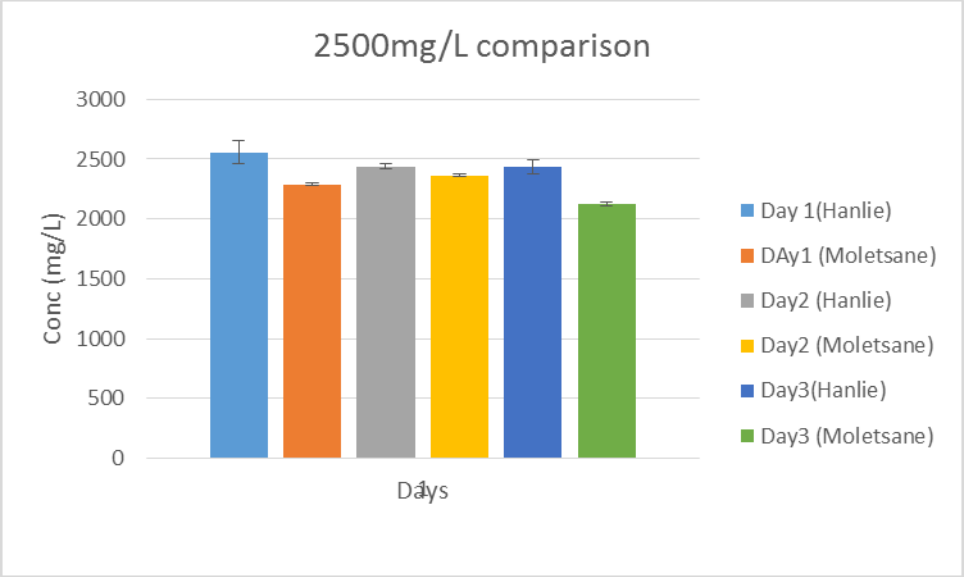


Figure D-2: AAS analysis (2500 mg/L)

From Figure D-2 it can be seen that, as the concentration was increased to a higher value of 2500mg/L aluminium, the ability of the AAS to accurately detect metal ions also increased. This was evident from the above graph for a number reasons. Firstly the average values of both operators were found to be in the same region (2300-2500mg/L) albeit that those of operator 2 (Moletsane) were on average still slightly less. There was a marked increase in both the operators' accuracy and precision with the higher concentration value.

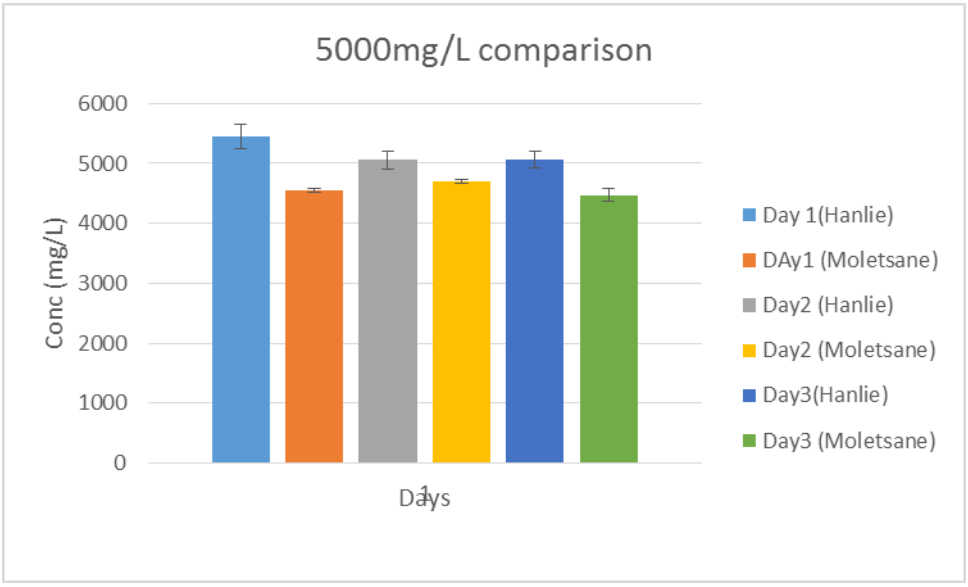


Figure D-3: AAS analysis (5000 mg/L)

Figure D-3 investigates the analysis of the AAS using a concentration of 5000 mg/L.The highest concentration tested (5000mg/L) bears the same characteristics and trends to those discussed for the medium (2500mg/L) concentration. This indicated that the AAS was less accurate at the low spectrum of concentrations.

Lastly, a few observations and comments on the AAS in general. These observations serve to also explain why the daily concentrations of the operator changed as well as why both operators had slightly different concentration ranges were found to be as follows;

Firstly, it was found from the analytical laboratory staff that a 2 – 3% variation in results on an analytical instrument is normal. In terms of the AAS specifically, results from an acetelyne/air flame will always be more consistent than from a nitrous oxide/acetylene flame. The aluminium concentration determining method used a nitrous oxide/acetylene

Secondly, when processing and analysing results, it is important to keep dilution and dilution factors in mind. When having a difference of say 1 – 2 ppm on the AAS during analysis, this difference, when applied by the dilution factor of samples, will jump to e.g. 10 – 20 ppm (10x dilution) or 100 – 200 (100x dilution) depending on the dilution made. And there will also be a percentage error in the dilution, which will be magnified accordingly as well. This needs to be kept in mind when processing different sets of results.

Another observation about the AAS machine was that the instrument required a fairly long warm-up time when using the nitrous oxide flame. This means it would have been necessary to calibrate at regular intervals to compensate for temperature effects. This proved to be very cumbersome and instead it was recommended that a quality control sample (with known concentration) be prepared and read after every 10th sample. If it changed, then only recalibrate the AAS then. This was subsequently done for all experimental analysis.

Lastly, as a final note on using nitrous oxide on the AAS, it was found that the burner easily became clogged. The burner was subsequently regularly checked and cleaned if necessary. The same was applied to the sampling line.

Appendix E: Experimental conditions in case study

Appendix E provides a list of experimental conditions used by Miyoshi (1997) in his study on the effect of having different valence ions on the feed and sweep side of a DD and its effect on recovery.

Table E-1: List of experimental conditions for effect of valence investigation (Miyoshi, 1997)

	Cell 1			Cell 2		
Run no	Feed ions	Conc (kmol/m^3)	Feed ions	Conc (kmol/m^3)	Driving ions	Conc (kmol/m^3)
1*	Na^+	0.01	Na^+	0.01	H^+	1.0
2	Na^+	0.01	Na^+	0.01	H^+	1.0
3	Na^+	0.01	Na^+	0.01	H^+	1.0
4+	Na^+	0.01	Na^+	0.01	H^+	1.0
5	K^+	0.005	K^+	0.005	Na^+	1.0
6	K^+	0.01	K^+	0.01	Na^+	1.0
7	K^+	0.02	K^+	0.02	Na^+	1.0
8	K^+	0.03	K^+	0.03	Na^+	1.0
9	K^+	0.01	K^+	0.01	Na^+	1.0
10	K^+	0.01	K^+	0.01	Na^+	0.1
11	K^+	0.01	K^+	0.01	Na^+	1.5
12	K^+	0.01	K^+	0.01	Na^+	3.0
13	K^+	0.01	K^+	0.01	Na^+	5.0
14	K^+	0.01	K^+	0.01	H^+	1.0
15	Na^+	0.01	Na^+	0.01	K^+	1.0

16	Ca^{2+}	0.01	Ca^{2+}	0.01	Cu^{2+}	1.0
17	Ca^{2+}	0.01	Ca^{2+}	0.01	Mg^{2+}	1.0
18	Ca^{2+}	0.01	Ca^{2+}	0.01	Ca^{2+}	1.0
19	Cu^{2+}	0.01	Cu^{2+}	0.01	Mg^{2+}	1.0
20	Mg^{2+}	0.01	Mg^{2+}	0.01	Ca^{2+}	1.0
21	Mg^{2+}	0.01	Mg^{2+}	0.01	Cu^{2+}	1.0
22^{-}	Na^{+}	0.01	Na^{+}	0.01	K^{+}	1.0
23	K^{+}	0.01	K^{+}	0.01	Na^{+}	1.0
24	K^{+}	0.01	K^{+}	0.01	Na^{+}	1.0
25	K^{+}	0.01	K^{+}	0.01	Na^{+}	1.0
26	K^{+}	0.01	K^{+}	0.01	Na^{+}	1.0

The co ions used in Run 22 were SO_4^{2-} ions, in all other runs they were Cl^{-} ,secondly The rotation of the stirrer speed was 600rpm except for the subscripts *, + and - which denoted:300rpm,500rpm and 700rpm respectively.

Appendix F: Operating procedure for analysis machines

Appendix F-1 Atomic Absorption Spectroscopy (AAS)

The operating procedure used for the Atomic Absorption Spectroscopy (AAS) machine is provided below.

AAS Start-up

The AAS machine is switched on. The cylinders of Argon, nitrogen and air are opened to feed to the AAS machine. After this, machine is initialized and the analysis flame is switched on. The machine is left to warm up for 6 minute

AAS Operation

After the 6 minute burn in, the AAS machine is calibrated with 5 aluminium standards of 2ppm, 10ppm, 25ppm, 50ppm and 100ppm in order to produce a calibration curve. The Donnan Dialysis samples obtained from the runs are fed to the machine for analysis.

It should be noted that some of the samples need to be diluted in order to be in the readable concentration range of the AAs machine, which is from 0 to 100 ppm aluminium. The standards which have a higher concentration that this range are diluted accordingly using distilled water.

Shutdown

Once the analysis is done, the cleaning chamber of the machine is cleaned, then the analysis flame is extinguished. The Nitrogen, air and Argon cylinders are then closed.

Appendix F-2 Ultra violet visible Spectrophotometer

The operating procedure used for the Ultra violet visible Spectrophotometer is provided below.

UV-vis Startup

The machine is switched and left to warm up for 12 hours before use. Two quartz cuvettes are wiped thoroughly with cloth to ensure no fingerprints are on them. Distilled water is added to the first and inserted in the machine in order to initialize the machine and have the reference point of pure water.

UV-vis Operation

Once the machine has been initialized, samples are added to the second cuvette which is also placed in the UV-vis machine. The desired wavelength for analysis is selected (UV 254nm) and then each sample is then analyzed individually. The cuvette is rinsed with distilled water and wiped before each new sample is poured into the cuvette for analysis.

UV-vis Shutdown

The two cuvettes are taken out of the machine and the machine is switched off. The cuvettes are rinsed with distilled water and dried using a cloth.

Appendix F-3 Equipment leak testing

The presence of leakages results in a loss of both feed and sweep solution which then leads to experimental results being incorrect. The most common sources of leaks on the apparatus have been listed below:

Improper sealing and connecting of the Teflon pipes to the pumps.

- A tear in the Teflon pipes.
- Improper sealing and connecting of the Teflon pipes to the PVC blocks.
- The silicon rubber in between the PVC blocks not placed properly.
- A tear in the membrane.
- The PVC blocks not screwed together tightly enough.
- A tear in the peristatic pumps inner tubing.

The simplest way to test for these leakages is by filling both the feed and sweep containers with 3L of water. Switch on only the feed side pump for an hour. After the hour if there is still 3L of water in the feed side and 3L in the sweep side then there are no leaks on the feed side. If however, the feed side has decreased in volume and the sweep side has increased in volume it means the membrane has a tear. The last possibility is if the feed volume has decreased but the sweep volume has not. This means that there is a leak somewhere in the apparatus such as the pipes or nozzles that needs to be fixed. Once this exercise has been done for the feed side, it is repeated for the sweep side.